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THE ALIPHATIC FREE RADICALS

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THE
ALIPHATIC FREE RADICALS

BY

F. O. RICE AND K. K. RICE
The Johns Hopkins University

With a Foreword
BY
F. A. PANETH

BALTIMORE
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FOREWORD

Technical disputes which rage for long between leading scientists seldom admit of a final decision; even the complete victory of one side usually tends merely to a temporary settlement, for sooner or later the opposite view again comes into favour, thus necessitating a finer distinction between right and wrong. Hence the protraction of the struggle: " Les querelles ne dureroient pas longtemps, si le tort n'étoit que d'un côté," as La Rouchfoucauld says. Examples of such contests are shown in physics in the arguments between the protagonists of the wave, and of the emission, theories of light; and in chemistry, over the existence of free carbon-hydrogen radicals. A significant indication of the direction in which contemporary chemistry is developing is the appearance today of F. O. Rice and K. K. Rice's book on free aliphatic radicals, dealing with many questions previously regarded as finally solved by the defeat of the old " radical theory."

But how different is the modern formulation of the problem! Historically we know what great importance chemists of a hundred years ago attached to the decision as to whether free radicals existed or not, and how vehemently they sought for evidence and counter-evidence. The extremes to which the controversy was carried is exemplified by Laurent's declaration that, given proof of a single free radical, he would admit all the rest by analogy.

Today we adopt a quite different and far more dispassionate attitude. We feel that the original problem was too categorically stated, and that we cannot insist on radicals being demonstrated as stable gases before we accept their chemical importance. We no longer ask: " Do radicals exist? " but rather: " How long can this radical remain in the free state under such and such conditions? " Nor do we dream of relying on analogical conclusions, for we now know that the life of free radicals can vary from easily measurable, to imperceptibly short, periods of time.

The satisfactory proof of the existence of single free radicals does not therefore imply for us a final yes or no verdict, but rather an opening up of new and often tedious fields of research. The older chemists seem now not only too exacting in their claims but also inadequate in their test-methods. In striking contrast to the then advanced aim of producing the radicals of organic chemistry with as much exactitude as the inorganic chemical elements, must appear the easy conviction which permitted even Bunsen and Frankland to explain radical twins as free radicals, in spite of density determinations contradictory to Avogadro's Law. Today in every single instance we demand definite proof of the independent existence of the real radical over a certain limited period of time.

This new "radical theory" is capable of interesting application in various branches of chemistry. Undoubtedly important is its extension to the field of reaction kinetics, in which, as is well known, the senior author of this book has been so successfully occupied for many years. Earlier theoretical deductions are now given a firm experimental basis, and complicated reactions can in many cases already be kinetically explained in all their details.

With the help of improved technique recent work on free radicals offers simultaneously a clarification of older questions and a stimulus to further investigation. I therefore value this treatise from a two-fold standpoint: for its clear compilation of work done up to date, and for its indication of the trend of future research; and as such it will surely be welcome and very useful to many. I think that this is an especially opportune moment for the publication of a work which presents so thoroughly the experimental and theoretical sides of the problem.

F. A. PANETH

London, November, 1934

PREFACE

Paneth's discovery of the free methyl radical in 1929 served as the impetus for the initiation of a rather considerable amount of experimental work, as the result of which evidence is now accumulating in support of the theory that the final products of many reactions are obtained not directly but through a series of steps involving a dissociation into free radicals followed by a radical chain. A few years ago it was hardly possible seriously to entertain such a view of the mechanism of organic decompositions, and even now it is not possible to point to definite and incontrovertible proof that free radicals enter into pyrogenic changes in general; and while the chemistry of radicals will be studied in any case, it is quite clear that their importance will depend to a large extent on how far they enter into ordinary thermal decompositions.

In this book we have given an account of the preparation and properties of those aliphatic free radicals that have been discovered and studied during the past few years. In addition we have presented hypothetical free radical mechanisms for the thermal decomposition of numerous aliphatic compounds. Presumably within only a very few years the mechanisms will have been either disproved or confirmed. At present the entire subject is in a very early and necessarily controversial phase of its development and we can only indicate the direction of the drift of the evidence now available. We hope that the material we have collected will be of service to those physical, organic, and biological chemists now working in this field, and that it may also interest others in problems connected with the study of the mechanism of organic reactions.

The authors wish to thank Dr. A. H. Corwin, Sr. M. Denise Dooley, Dr. M. Goeppert-Mayer, Dr. Karl F. Herzfeld, Dr. J. E. Mayer, Dr. E. E. Reid and Dr. H. S. Taylor for help in connection with reading and criticizing the manuscript.

F. O. Rice
K. K. Rice

Baltimore, Maryland, December, 1934

CONTENTS

PAGE

CHAPTER I. INTRODUCTION 13

CHAPTER II. EARLY HISTORY 21

- Cyanogen, benzoyl, etherin and cacodyl radicals 21
- Early attempts to prepare methyl and ethyl radicals 22
- Abandonment of the Search for Free Radicals 23
- Discovery of Free Aryl Radicals 23

CHAPTER III. HISTORICAL. 1912-1934 25

- Photochemical Dissociation 25
- Induced Polymerisation of Ethylene 25
- Photochemical Dissociation of Aldehydes and Ketones 26
- Photochemical Dissociation of Alkyl Iodides 28
- Hydrogen Atoms and Hydrocarbons 30
- Alkali Metal Atoms and Organic Halides 31
- Free Methyl Radical 31
- Decomposition of Organic Compounds into Radicals 32
- Initiation of Chains by Free Radicals 35

CHAPTER IV. PREPARATION AND IDENTIFICATION 36

- Original Paneth Method 36
- Use of Condensable Gases 39
- Free Radicals from Non-metallic Organic Compounds 41
- Preparation of the Methylene Radical 41
- Production of Free Radicals in a Discharge Tube 42
- Reaction between Sodium Vapor and Alkyl Halides 43
- Identification of Free Radicals 44
- Identification of the Methylene Radical 51
- Identification of Hydrogen Atoms 54

CHAPTER V. PROPERTIES AND REACTIONS 55

- Measurement of Life of Radicals 55
- Reactions with Solid Substances 57
- Temperature Coefficient of Reaction with Metals 60
- Products Formed by Reaction with Metals 61
- Decomposition and Interaction of Free Radicals 62
- Reactions of Free Radicals with Olefins 67
- Reactions of Free Radicals with Organic Molecules 69
- Bivalent Radicals 70

CHAPTER VI. ACTIVATION ENERGIES OF ELEMENTARY REACTIONS . . . 72

- Thermo-chemical Estimates of Bond Strengths 72
- Effect of Substitution and Structure on Bond Strength 75
- Activation Energies from Kinetic Measurements 77
- Decomposition of Radicals 79

PAGE
Interaction of Radicals and Organic Molecules 80
Interaction of Radicals with Each Other 82
Activation Energies of Migration Processes 83
Calculation of Rates of Elementary Reactions 84
Pattern Reactions 86

CHAPTER VII. PARAFFIN HYDROCARBONS 91
Methane 91
Ethane 91
Propane 92
Isobutane 94
n-Butane 94
Pentanes 95
Effect of Temperature and Pressure on Products 100

CHAPTER VIII. KETONES AND ALDEHYDES 108
Acetone 109
Methyl Ethyl Ketone 109
Diethyl Ketone 110
Methyl Propyl Ketone 111
Methyl isopropyl Ketone 111
Pinacolone 111
Acetaldehyde 112
Propionic Aldehyde 112

CHAPTER IX. ETHERS 114
Dimethyl Ether 115
Methyl Ethyl Ether 115
Diethyl Ether 115
Methyl isopropyl Ether 116
Di-isopropyl Ether 117
Di-tert. butyl Ether 117

CHAPTER X. OLEFINIC HYDROCARBONS 120
Effect of Double Bond on Reactivity with Radicals 120
Allyl Type of Free Radical 121
Propylene 123
Butene-1 125
Isobutylene 127
Pentenes and higher Homologues 129

CHAPTER XI. OTHER ORGANIC COMPOUNDS 134
Alcohols 134
Fatty Acids 135
Dibasic Acids 136
Chlorine Derivatives 137
Alkyl Nitrites 138
Aliphatic Azocompounds 140

PAGE

CHAPTER XII. LARGER MOLECULES 142

Hexadecane 142
Hydrocarbons with Recurring Units 145
Non-volatile Organic Compounds 147
Sulfur Polymers 148
Rubber Hydrocarbon 152
Polymers with Unsaturated Side Chains 154

CHAPTER XIII. ALICYCLIC COMPOUNDS 159

Structure of Alicyclic Compounds 159
Cyclopropane 160
Ethylene Oxide 161
Cyclopentane 162
Cyclohexane 163
Pinene 163

CHAPTER XIV. REACTIONS IN THE LIQUID PHASE 165

Effect of Temperature on Relative Rates 165
Effect of Solvent on Dissociation Processes 165
Oxidation of Sodium Sulfite 166
Haber-Willstatter Chain Mechanism 170
Cannizzaro Reaction 171
Nature of Enzymes 171
Oxidation of Ethyl Alcohol 172
Oxidation of Acetaldehyde 173
Disproportionation of Aldehydes 173
Dehydrogenation of Succinic Acid 175
Mechanism of Peroxidase Catalysis 175
Catalase Decomposition of Hydrogen Peroxide 176
Alcohol Reactions 176
Aldehyde Reactions 178
Addition of Halogen Acids to Olefins 181

APPENDIX I. Activation Energies of Unimolecular Elementary Reactions . 183

APPENDIX II. Activation Energies of Elementary Bimolecular Reactions . 189

INDEX OF NAMES 193

INDEX OF SUBJECTS 197

CHAPTER I

INTRODUCTION

The chief interest and importance of alkyl radicals lies in the possibility that they are the fugitive intermediaries in chemical change: that chemical reactions really proceed through a free radical mechanism. In this book we hope to show that it is possible to set up a reasonable mechanism which enables one to predict the products of organic pyrogenic decompositions both qualitatively and quantitatively for the different classes of aliphatic compounds. The close agreement between the products predicted on the basis of a free radical mechanism and the products found by experiment for a great many different types of organic compounds makes somewhat plausible the assumption that the energy necessary to cause two organic molecules to react in a bimolecular collision or to cause rearrangement of an organic molecule to give the products directly is in general greater than the overall energy of a dissociation into fragments followed by a chain reaction.

Until very recently free radicals have played practically no part in the development of organic chemistry. With the advent of the theory of valence in 1858 the postulate of the quadrivalence of carbon was made the foundation of the whole of structural organic chemistry. Indeed, owing to the success of the application of the valence theory to the carbon compounds, Kekulé was led to infer that valence was a definite and unalterable property of each atom.

Practically every organic text book written prior to 1930 contains a statement that free radicals are incapable of an independent existence. The following, taken from Richter's Organic Chemistry, p. 24 (1915), is a typical statement: " The assumption of the existence of radicals, capable of existing alone and playing a special *role* in molecules has long been abandoned." The proof of the existence of the free methyl group by Paneth and Hofeditz in 1929 is sufficiently important that it may be justly said to necessitate a complete reconsideration of the mechanism of organic reactions. Although only very few free radicals have been prepared by the original method of Paneth and Hofeditz, and although it appears that larger alkyl radicals are too unstable to be prepared by this method, nevertheless there exists a considerable body of strong presumptive evidence indicating that a great variety of radicals have an independent existence and play an important rôle in the mechanism of chemical change.

The free alkyl radicals so far prepared have been found to have a half life of a few thousandths of a second; it is obvious therefore why the methods of classical organic chemistry were powerless to study, or even to detect, the existence of fragments of such fugitive existence. It is true that for a long time past physicists have made very complete studies of the properties of very short-lived particles; but these studies were only possible either when the particles were sufficiently highly excited that they emitted light, or when they were charged, in which case they could be affected by electric and magnetic fields. Neither of these methods is available for the study of free radicals because a chemical reaction occurring even at 1000° C. has not enough energy to cause the production of ionized fragments.

One of the earliest successful attempts to isolate and study active fragments was made by Langmuir in his studies of atomic hydrogen;[1] he found that a wire of tungsten, platinum, or palladium heated above 1000° C. in hydrogen at very low pressures, causes the hydrogen to dissociate into hydrogen atoms; these diffuse away from the heated wire to a considerable distance; their presence can be shown by the reduction of various metallic oxides, and by their reactivity at room temperature with such substances as oxygen and phosphorus. Atomic hydrogen can also be drawn out of a discharge tube[2] and its presence detected at considerable distances; quantitative measurements based on the heat of recombination[3] have shown that in some experiments the hydrogen was still over 25% dissociated at a distance of 100 cms. from the discharge tube. A number of studies of the reactions of atomic hydrogen[4] produced by Wood's method have now been made. Similar work with a water vapor discharge tube indicates that the hydroxyl radical may be prepared[5] by an analogous method.

In all of these methods the atom or molecular fragment is produced at low pressure by heat or an electrical discharge and then swept rapidly out of the decomposition zone; its presence is demonstrated through its great chemical reactivity. This is essentially the principle of the method used for studying the free radicals produced in the decomposition of organic compounds. The organic compound is passed through a furnace at low pressures; the furnace is heated to the temperature at which the compound decomposes; an inert carrier gas may or may not be used. The undecomposed original compound together with any fragments formed, pass rapidly to a cold part of the tube where the fragments may be identified by the compounds they form with a metal. The curious property of free radicals of combining with metals may possibly be connected with the primary formation of an organo metal;[6] compounds such as ethyl mercury, CH_3CH_2Hg, possessing a high conductivity and metallic lustre, have been prepared; at room temperature these compounds decompose into the dialkyl mercury and metallic mercury.

---

[1] Langmuir, *J. Am. Chem. Soc.*, 34, 1310 (1912); Freeman, *ibid.*, 35, 927 (1913); Langmuir and Mackay, *ibid.*, 36, 1708 (1914).

[2] R. W. Wood, *Proc. Roy. Soc.*, A97, 455 (1924); 102, 1 (1925).

[3] Smallwood, *J. Am. Chem. Soc.*, 51, 1985 (1929).

[4] See Urey and Lavin, *J. Am. Chem. Soc.*, 51, 3286 (1929) for a summary of this work.

[5] Urey and Lavin, *J. Am. Chem. Soc.*, 51, 3290 (1929); Lavin and Jackson, *ibid.*, 53, 3189 (1931); Harteck, *Trans. Far. Soc.*, 30, 139 (1934); Oldenberg, *J. Chem. Physics*, 2, 713 (1934).

The liberation of free radicals at electrodes has been shown in an ingenious manner by Hein and co-workers.[7] Zinc diethyl is a non-conducting liquid; it dissolves sodium ethyl to give a conducting solution due, presumably, to the equilibrium,

$$\mathrm{Na\,CH_2CH_3} \leftrightarrows \mathrm{Na^+} + \mathrm{CH_3CH_2^-},$$

and on passing a current through the solution the free ethyl radical should be liberated at the anode. Using platinum, copper, iron or tantalum anodes, ethylene and ethane are the chief products, presumably due to the reaction $2\,C_2H_5 \rightarrow C_2H_4 + C_2H_6$, although some butane is also formed. On the other hand, when a lead anode is used, only drops of lead tetra-ethyl are formed: $4\,C_2H_5 + Pb \rightarrow Pb(C_2H_5)_4$. The organo metallic compound is also formed with a wide variety of metals such as zinc, antimony, aluminium, bismuth, thallium, gold and tin accompanied to a greater or less extent by the products of interaction of the radicals with themselves. Similar results are obtained[8] when an ethereal solution of an ethyl magnesium halide is electrolysed.

There also exists a considerable body of results obtained by classical methods pointing to the fugitive existence of free radicals. For example, Staudinger and Kupfer[9] passed carbon monoxide through an ethereal solution of diazomethane $CH_2{=}N{\equiv}N$; the gaseous mixture was then passed, at atmospheric pressure, through a furnace heated in the range 400-500° C., and ketene was identified among the products. Staudinger and Kupfer represent the reaction as the separation of the CH_2 group from the nitrogen, followed by reaction with CO to give ketene $CH_2{=}CO$; however, according to the classical explanation there is a simple bimolecular reaction between carbon monoxide and diazomethane, resulting in nitrogen and ketene, without the intermediate formation of a free radical. Steacie[10] has recently shown that under certain conditions diazomethane decomposes into nitrogen and ethylene according to a bimolecular law.

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[6] Kraus, *J. Am. Chem. Soc.*, **35**, 1732 (1913); Rice and Evering, *ibid.*, **56**, 2105 (1934).

[7] *Z. anorg. Chem.*, **141**, 161 (1924); **158**, 153 (1926).

[8] Evans and Lee, *J. Am. Chem. Soc.*, **56**, 654 (1934); see also Wooster, *Chem. Reviews*, **11**, 1 (1932).

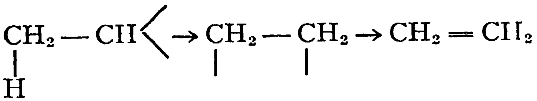
[9] Staudinger and Kupfer, *Ber.*, **45**, 508 (1912).

Free radical formation has frequently been discussed in connection with the thermal decomposition of organic compounds[11] but usually not in any detail; for example Bone and Coward[12] suggest that the rupture of bonds to give free radicals would explain the results of their experiments on the decomposition of hydrocarbons. They state: " One of the principal factors operative at 800° C. and higher temperatures is the direct hydrogenation of such residues as CH, CH_2 and possibly CH_3 (which conceivably have a momentary separate existence during the dissolution process) to methane whenever the atmosphere is rich in hydrogen. In this and in no other way can the phenomenally large production of methane during the decomposition of the other three hydrocarbons be accounted for."

Moreover, Nef[13] explained a great variety of chemical reactions on the basis of a free radical mechanism; in general, he represented a decomposition as a rupture to give a smaller molecule and a radical containing bivalent carbon. For example, he represented the thermal decomposition of ethane or an alkyl halide as involving the primary formation of the ethylidene radical:

$$C_2H_6 \rightarrow CH_3CH + H_2$$
$$CH_3CH_2X \rightarrow CH_3CH + HX$$

when X represents a halogen atom. The ethylidene radical was then supposed to undergo a rearrangement as follows:[14]



$$\underset{\substack{|\\ H}}{CH_2}-CH< \;\rightarrow\; \underset{|}{CH_2}-\underset{|}{CH_2} \rightarrow CH_2=CH_2$$

---

[10] Steacie, *J. Phys. Chem.*, 35, 1493 (1931).

[11] Hurd, *Pyrolysis of Organic Compounds*, pp. 55, 64, 70, 74, 83, 95, 110, 224, 231, 579, Chemical Catalog Co., 1929.

[12] Bone and Coward, *J. Chem. Soc.*, 93, 1197 (1908).

[13] Nef, *Ann.*, 298, 202 (1897).

[14] Nef, *Ann.*, 318, 16 (1901).

Nef used this type of mechanism in the explanation of a great variety of organic reactions;[15] that is, an alkylidene radical was formed in the primary reaction by the splitting off of hydrogen, water, halogen acid, etc. according to the type of compound used.

The evidence of the first step of the Nef mechanism, namely alkylidene formation, will be discussed later. We wish to point out here that the succeeding steps as postulated by Nef are quite impossible if our present knowledge of the strengths of bonds in organic molecules is even approximately correct. He represented the decompositions of acetaldehyde and acetone respectively as:

$$CH_3CHO \rightarrow CH_2 + HCHO \rightarrow CH_2 + 2H + CO \rightarrow CH_4 + CO$$

and:

$$\begin{aligned} CH_3COCH_3 &\rightarrow CH_2 + C\overset{*}{H}_3CHO \rightarrow 2CH_2 \\ &+ HCHO \rightarrow 2CH_2 + 2H + CO \rightarrow CH_4 + CO + CH_2. \end{aligned}$$

Such reactions as these may be important in the temperature range 2000-4000° C., but they can hardly occur to an appreciable extent in the ordinary range (500-700° C.) used in studying such thermal decompositions. With the limitation imposed on us by reaction kinetics and by our knowledge of bond strengths, it does not seem possible to devise a satisfactory mechanism involving primary alkylidene formation for many organic decompositions. Thus, it is known now that when acetone is decomposed[16] to only a small extent, ketene and methane are practically the only products:

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO.$$

This reaction could conceivably occur through transference of a hydrogen atom from one carbon atom to another with the direct formation of the products; or it could occur through a chain reaction initiated by the rupture of a C-C bond (see Chapter VIII); but we have been unable to devise any satisfactory scheme involving the primary formation of a bivalent radical to account for the products.

In spite of the fact that this mechanism seems improbable when applied to many organic compounds, the decomposition of methane has recently been interpreted[17] according to Nef's scheme of primary alkylidene formation: $CH_4 \rightarrow CH_2 + H_2$, and the observed kinetics of the methane decomposition seem to agree with a scheme based on this as the primary reaction.

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[15] Ref. (11), p. 766, Nef references.

[16] Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

[17] Kassel, *J. Am. Chem. Soc.*, **54**, 3949 (1932); see however Rice and Dooley, *ibid.*, **56**, 2747 (1934).

Recent calculations[18] appear to show that bivalent carbon is formed very easily; for example, according to these calculations, the energy required to dissociate CH_3 to CH_2 is only 25 Cal. If these calculations are correct they would afford very strong support for Nef's mechanism based on bivalent carbon. On the other hand there is now considerable experimental evidence to show that the free methyl group is very stable[19] and that the separation of another hydrogen atom to give the methylene group probably requires 80-100 Cal.; further confirmation of this was obtained[20] when it was found that above 700° C. a methylene group produced from diazomethane in ether picks off a hydrogen atom from surrounding molecules of ether and forms a methyl group. On this basis the production of bivalent carbon radicals could occur only to a negligibly small extent in normal chemical decompositions; we will, therefore, not consider in detail any reaction mechanism based on the formation of bivalent carbon.

In recent kinetic studies, and especially in recent photochemical studies, of organic reactions the assumption of dissociation into free radicals has been made more definitely. Thus Hinshelwood[21] represented the decomposition of acetone as the "separation of carbon monoxide from the molecule, leaving two methyl residues, the interaction of which determines the other products." Similarly, he represents[22] the decomposition of diethyl ether as

$$CH_3CH_2—O—CH_2CH_3 \rightarrow CO + \left[\begin{pmatrix} CH_5 \\ C_2H_5 \end{pmatrix} \rightarrow 2CH_4 + CH_2 \right],$$

assuming a rapid combination of the CH_2 residues to give ethylene. Taylor[23] has discussed processes involving the formation of ethylene, atomic hydrogen and free methyl and ethyl groups in considerable detail. In particular he emphasizes the possibility that the formation of a free radical may initiate a chain reaction. There is also the very important work of Polanyi and his co-workers [24] on reactions in very dilute flames. A stream of sodium vapor was allowed to mix with the vapor of a wide variety of organic halides at very low pressures; the authors state definitely that free radicals are formed by the splitting off of the halogen atom from the organic compound.

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[18] Mecke, *Z. Elektrochem.*, 36, 589 (1930).

[19] Paneth and Lautsch, *Ber.*, **64**, 2715 (1931); Rice, *J. Am. Chem. Soc.*, **56**, 488 (1934).

[20] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).

[21] Hinshelwood, *Proc. Roy. Soc.*, A, **111**, 245 (1926).

[22] Hinshelwood, *Proc. Roy. Soc.*, A, **114**, 84 (1927).

[23] Taylor, *Proc. Am. Phil. Soc.*, **65**, 90 (1926).

The kinetic studies of the thermal decomposition of organic compounds [25] must necessarily have an important influence on our ideas concerning the production of free radicals. The experimental fact that a wide variety of organic compounds decompose homogeneously and according to a unimolecular law predisposes us in favor of a mechanism consisting of an intramolecular rearrangement followed by dissociation into two molecules. Such a mechanism appears more reasonable than free radical formation, since the latter might be expected to initiate reaction chains and make the kinetics of the decomposition more complicated.

During the years 1925 to 1930 there was an increasing tendency in photochemical studies to postulate primary processes involving the dissociation of a molecule into atoms or other fragments. At the Faraday Symposium [26] in 1925 such mechanisms were put forward mainly in connection with the photochemical reactions of inorganic compounds. However, it was natural that these same ideas should be applied to analagous studies of organic compounds, and a few years later we find a number of papers [27] in which the photochemical dissociation of organic compounds into free radicals is worked out in considerable detail.

The question of the strength of bonds in organic molecules is extremely important in connection with the possibility of the production of free radicals. This fact has long been recognized by organic chemists and many attempts have been made to measure the relative strengths of bonds in organic molecules.[28] These measurements, which have usually been made in connection with electron theories of valency, enable us to make rough estimates of the relative strengths of binding [29] of different radicals.

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[24] Beutler and Polanyi, *Naturwissenschaften*, **13**, 711 (1925); Hartel and Polanyi, *Z. physik. Chem.*, **11 B**, 97 (1930); Hartel, *Trans. Far. Soc.*, **30**, 187 (1934); Horn, Polanyi and Style, *ibid.*, **30**, 189 (1934).

[25] See Rice, *Chem. Reviews*, **10**, 135 (1932) for a summary of this work.

[26] *Trans. Far. Soc.*, **21**, 438 (1925).

[27] *Trans. Far. Soc.*, **27**, 383, 387, 391, 392, 404, 409, 468 (1931); Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

[28] See Lucas, *J. Am. Chem. Soc.*, **48**, 1831 (1926); Kharasch and Marker, *ibid.*, **48**, 3130 (1926).

[29] A summary of this is given in ref. (8), p. 38.

The problem of determining the binding strength of the different types of bonds in organic molecules will be discussed in detail in Chapter VI. The problem here is to determine the energy associated with the rupture of a bond in an organic molecule resulting in the formation of two uncharged, unexcited fragments. Fortunately a number of methods of measurement are now available, although the results obtained by different methods are not very concordant.

Actually, of course, our interest in the strengths of bonds in organic molecules is the result of the information we can thus obtain regarding the activation energy, not only of the primary decomposition, but also of the subsequent reactions between the free radicals and the original compound. The bond strengths give us minimum values for the activation energies; furthermore it is probably justifiable to assume a parallelism between bond strengths and activation energies. The mechanism of even a very complicated organic decomposition would immediately become clear if we knew the exact values of the activation energies of all the reactions that might occur. Although at present our knowledge is very limited and uncertain in this respect, we hope to show in the following pages that it is possible, using reasonable estimates for these quantities, to set up mechanisms for organic decomposition, which involve, in most cases, free radical formation and which are in agreement with experimental results.

CHAPTER II

EARLY HISTORY

We owe the term "radical" to Lavoisier; he included "simple radicals" (i. e. elements) as well as "compound radicals" in his definition and pointed out[1] that the inorganic radicals are usually elementary, whereas the organic radicals are composed of at least two substances, carbon and hydrogen, and that frequently phosphorus and nitrogen are also included. Much of the subsequent work in organic chemistry was concerned with the nature and reactions of radicals and especially with attempts to secure them in the free state; the similarity between the "compound radicals" and the "simple radicals" or elements seemed to indicate that the former must also exist in the free state. In 1815 Gay-Lussac[2] prepared pure prussic acid and established its constitution as HCN; he succeeded in isolating its compound radical as a gas, which he called cyanogen. It seemed therefore to the chemists of that time that for the first time a free radical had been isolated. After this, the knowledge of organic radicals advanced rapidly, chiefly owing to the development of satisfactory methods of organic analysis begun in 1810 by Gay-Lussac and Thénard.[3]

The classic researches of Liebig and Wöhler on the benzoyl radical, in 1832, also had great influence on the chemical thought of the time.[4] Starting with oil of bitter almonds (benzaldehyde), they showed that it could be converted into a series of related compounds, all of which contained the group C_7H_5O. A short time after the publication of this paper, Laurent[5] claimed, with some slight reservations, to have prepared the free benzoyl radical: he had really, of course, obtained dibenzoyl or benzil.

Some time previously Dumas and Boullay[6] had suggested that alcohol, its esters and ether could all be considered as derivatives of ethylene and Berzelius,[7] even suggested that ethylene be called the "etherin radical." Alcohol and ether were explained as compounds of this radical with water. Liebig,[8] however, showed that the radical in question had the composition C_2H_5, and even went so far as to predict the possible isolation of the alkyl radicals through the action of potassium on their chlorides or iodides.

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[1] *Traité élémentaire de Chimie*, I, 209 (1793).

[2] Gay-Lussac, *Ann. chim.*, **95**, 156 (1815).

[3] See Kekulé, *Organische Chemie*, Vol. I, p. 18 (1867).

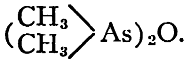
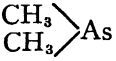
[4] Liebig and Wöhler, *Ann.*, **3**, 282 (1832).

[5] Laurent, *Ann. Chim.*, **59**, 397 (1835).

[6] Dumas and Boullay, *Ann. chim. phys.*, **37**, 15 (1828).

[7] Berzelius, *Ann.*, **3**, 282 (1832).

[8] Liebig, *Ann.*, **9**, 1 (1834).

About 1840 Bunsen commenced his researches on Cadet's fuming liquid[9] and separated cacodyl oxide  $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!As\right)_2O$. From this a whole series of derivatives was prepared, all of which retained the complex  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!As$ unchanged. Finally, by treating cacodyl chloride with zinc, cacodyl itself was liberated. It seemed therefore that another example could be added to cyanogen, of a compound radical isolated in the free state. In connection with his experiments with cacodyl, Bunsen also attempted to obtain alkyl radicals by heating alkyl chlorides with metals.[10] These experiments were not successful but some years later, in Bunsen's laboratory, Frankland[11] heated ethyl iodide with metallic zinc to 150° C. in a sealed glass tube. On opening the tube he found a gas with the empirical formula C_2H_5, which he regarded as the free radical ethyl. Actually, of course, he had prepared butane. At about the same time Kolbe[12] electrolysed acetic acid and obtained a gas which he regarded as free methyl (in reality ethane).

Shortly after the publication of Frankland's work three investigators, Gerhardt, Laurent, and Hofmann[13] independently expressed the opinion that both Frankland and Kolbe had been dealing, not with free radicals, but with " radical twins," and had in reality prepared butane and ethane. Neither Frankland nor Kolbe could be convinced of this. Even in Bunsen's laboratory at that time, Avogadro's rule was not recognized in practice; Frankland had gone so far as to determine the density[14] of his " free ethyl," stating that the density of " simple radicals " and " radical twins " should be the same.

Würtz[15] had also repeated the experiments of Frankland and of Kolbe, but using metallic sodium and alkyl iodides. When he used only methyl iodide or only ethyl iodide he obtained the simple radicals methyl and ethyl of Kolbe and Frankland; when he used mixtures of the two iodides he obtained mixed radicals as well, which he referred to as " methyl—ethyl."

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[9] Bunsen, *Ann.*, 37, 31 (1841).

[10] Bunsen, *Ann.*, 42, 45 (1842).

[11] Frankland, *Ann.*, 71, 171 (1849); 74, 41 (1850); 77, 221 (1851).

[12] Kolbe, *Ann.*, 69, 257, 279 (1849).

[13] *Jahresber. Chem.*, p. 345, 349 (1850).

[14] *Ann.*, 77, 239 (1851).

[15] Würtz, *Compt. rend.*, 40, 1285 (1854).

The following years were filled with disputes regarding not only the identity of these " free " radicals, but also the question of the independent existence of any free radicals. Liebig was convinced that organic chemistry could be defined as the chemistry of the compound radicals, whereas Laurent stated that the adherents of the radical theory had made chemistry a science of non-existing bodies.[16]

For a long time it was maintained that there were two series of paraffin hydrocarbons: one series consisting of " radical twins " and the other of the hydrides of the radicals; thus ethyl hydride, $C_2H_5 . H$ and di-methyl $(CH_3)_2$ were supposed to be isomeric. Even Baeyer's first work,[17] carried out in the Bunsen Institute, confirmed the difference between methyl chloride and chlorinated methane.

It was not until Schorlemmer [18] began his researches on the paraffin hydrocarbons that the matter was finally cleared up. He showed that the hydrocarbons of the two series underwent the same reactions and yielded the same products and that there was identity and not isomerism between the " radical twins " and the " hydrides." It was only then that free methyl and free ethyl were crossed from the literature.

From 1860 to 1900 the postulate of the quadrivalence of carbon was fully accepted and served as the basis for practically the entire development of organic chemistry during this period. The amazing development following the application of this postulate discouraged any further interest in free radicals and it seems to have been generally accepted [19] " that in the nature of radicals lies the explanation why they cannot be isolated."

It was not until the isolation of the free radical triphenylmethyl by Gomberg [20] in 1900 that interest in free radicals was revived. The observed cases of the dissociation of hexa-substituted ethanes have been limited to compounds containing at least two aryl groups attached to each of the carbon atoms; these separate in greater or less degree according to the character of the aromatic substituents. The substitution of the hydrogen atoms of ethane by bulky unsaturated alkyl radicals apparently weakens the central carbon–carbon bond but does not cause dissociation to occur; this has been shown for the compound hexa-tert-butylethenylethane[21] $((CH_3)_3CC{\equiv}C)_3C{-}C(C{\equiv}CC(CH_3)_3)_3$.

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[16] These disputes have their amusing side; as for example the invention (Laurent, *Méthode de Chimie*, p. 354 (1854)) of the imaginary radical "eurhyzen" represented by the symbol Eu, which fulfilled all the functions of a free radical, but when isolated in the free state turned out to be hydrogen peroxide. Also the publication by Liebig (*Ann.*, 33, 308 (1840)) of a letter signed with the suggestive name S. C. H. Windler, claiming to have successively replaced all the elements in manganese acetate with chlorine, with the result that the product, although consisting only of chlorine, had all the properties of the original salt.

[17] Baeyer, *Ann.*, 103, 181 (1857).

[18] Schorlemmer, *J. Chem. Soc.*, 16, 425 (1863); *idem, ibid.*, 17, 262 (1864).

[19] Ostwald, *Elektrochemie*, p. 625 (1896).

[20] Gomberg, *J. Am. Chem. Soc.*, 22, 757 (1900).

We may conclude therefore that the methods of classical organic chemistry are, except in isolated cases,[22] powerless to obtain aliphatic radicals in the free state or even to demonstrate with certainty their existence as fugitive intermediates in chemical change; it remains therefore to trace the development of physical chemical investigations which finally, through the discovery of the action of free radicals on metallic mirrors, led Paneth and his co-workers to the isolation of the free methyl and ethyl radicals.

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[21] Salzberg and Marvel, *J. Am. Chem. Soc.*, **50**, 1737 (1928).

[22] See *Trans. Far. Soc.*, **30**, pp. 10-102 (1934).

CHAPTER III

HISTORICAL—1912-1934

This period marks a revival of interest in the subject of free radicals which came about primarily through physical-chemical and photochemical investigations. The apparent failure of the Einstein Photochemical Law[1] stimulated interest in the mechanism of chemical change and gradually led to the realization that the quantum relation can only be applied to the primary change, and that secondary reactions or reaction chains sometimes cause great deviations when the law is applied in connection with the complete reaction. By 1925 the nature of the primary photochemical dissociation[2] was fairly well understood and considerable progress had been made in unravelling the extraordinarily complex series of reactions following the primary dissociation. Up to this time most of the investigations had involved the study of simple inorganic reactions such as the decompositions of HBr, HI, NH_3, O_3, H_2O_2, and the combination of H_2 and Cl_2, Cl_2 and CO etc.[3] Considerable evidence had accumulated that in numerous cases the secondary reactions are of the chain type. It is evident that similar considerations should apply to organic photochemical decompositions, and already in 1925 we find a chain mechanism involving a free ethyl radical[4] being postulated by Taylor. In his experiments, hydrogen atoms were produced in a mixture of ethylene and hydrogen at room temperature by illuminating the mixture, which contained a little mercury, with mercury resonance light. It was assumed that the hydrogen atoms thus formed react with the ethylene to produce free ethyl radicals, $H + C_2H_4 \rightarrow CH_3CH_2$; the ethyl groups then attack the hydrogen molecules, $CH_3CH_2 + H_2 \rightarrow C_2H_6 + H$, thus regenerating the hydrogen atoms, which continue the chain. Such a scheme would explain the experimental observation that more ethane is produced than would be expected from the number of hydrogen atoms originally produced. In this same paper Taylor also suggested that free ethyl radicals could be liberated in a hydrogen-ethylene mixture by adding a small quantity of a metal alkyl and heating to a temperature above that at which the metal alkyl decomposes but below the temperature at which hydrogen and ethylene react. Later when this experiment was carried out, it was shown[5] that when free methyl or ethyl groups from the corresponding mercury or lead alkyls are liberated in a hydrogen-ethylene mixture two reactions occur; the first reaction results in the formation of ethane and the second reaction in the polymerization of the ethylene; in the absence of metal alkyls no reaction of any kind occurs under the conditions of the experiment. The second reaction predominates, indicating that the free radicals produced react more readily with ethylene than with hydrogen.

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[1] Einstein, *Ann. Physik*, 37, 832 (1912).

[2] Franck, *Trans. Far. Soc.*, 21, 536 (1925).

[3] See *Trans. Far. Soc.*, 21, 444 (1925).

[4] Taylor, *Trans. Far. Soc.*, 21, 560 (1925).

The mechanism which Taylor proposed postulates the primary formation of free alkyl radicals, followed by successive reactions of the type, $CH_3CH_2 + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2$ to give the n-butyl radical; this in turn collides with another ethylene molecule to give the n-hexyl radical, and in this way the larger radicals can be built up. The disappearance of these larger radicals to form olefin hydrocarbons is supposed to be due to such reactions as:

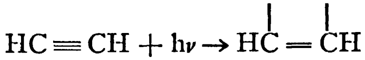
$$CH_3CH_2CH_2CH_2CH_2CH_2 + CH_3CH_2 \rightarrow C_2H_6 + CH_3CH_2CH_2CH_2CH = CH_2 \qquad 1$$

or

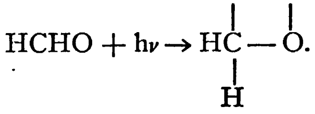
$$CH_3CH_2CH_2CH_2CH_2CH_2 + CH_2{=}CH_2 \rightarrow C_2H_5 + CH_3CH_2CH_2CH_2CH = CH_2. \qquad 2$$

The free radicals should finally disappear either through reaction 1 or by recombination on the wall.

Mecke[6] has suggested that the action of light in photochemical reactions is to cause a partial splitting of double or triple bonds thus leaving two free valencies:



$$HC \equiv CH + h\nu \rightarrow \overset{|}{H C} = \overset{|}{C H}$$



$$HCHO + h\nu \rightarrow \underset{\underset{H}{|}}{\overset{|}{HC}} - \overset{|}{O}.$$

This process can then be followed by reaction with oxygen or other substances. However, a dissociation process is also postulated[7]; in the case of formaldehyde three primary dissociation processes are suggested:

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[5] Taylor, *Proc. Am. Soc.*, **65**, 90 (1926); Taylor and Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

[6] Mecke, *Trans. Far. Soc.*, **27**, 374 (1931); see also Bodenstein, *Sitzb. preuss. Akad. Wiss.*, **3** (1931).

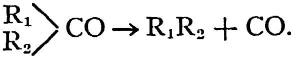
[7] Mecke, *Nature*, April 5 (1930); Herzberg, *Z. physik. Chem.*, B **10**, 189 (1930).

$$HCHO \rightarrow H + HCO; \tag{1}$$

$$HCHO \rightarrow H_2 + CO; \tag{2}$$

$$HCHO \rightarrow CH_2 + O; \tag{3}$$

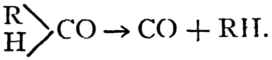
Mecke favors the first of these and considers that the HCO radical is very unstable and requires practically no energy to dissociate it further. On the other hand, Norrish[8] thought the second mechanism the most probable,[9] by analogy with the photochemical decomposition of unsymmetrical ketones, the decomposition of which may be represented as:



$$\left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle CO \rightarrow R_1R_2 + CO.$$

A general survey of the literature[10] indicates that carbonyl compounds decompose almost exclusively in this manner and that secondary changes do not account for more than 10% of the products. This would seem to be very convincing evidence that free radicals are not formed in the primary photochemical decomposition since if they were present we would expect to find R_1R_1, and R_2R_2, as well as polymers of the radicals R_1CO and R_2CO, among the products.[11]

Similarly the photochemical decomposition of both benzaldehyde and acetaldehyde[12] produces carbon monoxide, accompanied respectively by benzene and methane, according to the following equation:



$$\left.\begin{matrix}R\\H\end{matrix}\right\rangle CO \rightarrow CO + RH.$$

If dissociation into free radicals occurred we should expect benzene, diphenyl, and hydrogen as well as carbon monoxide from the decomposition of benzaldehyde, and methane, ethane, and hydrogen, in addition to carbon monoxide, from acetaldehyde. Thus the chemical evidence seems to point strongly to a photochemical dissociation of compounds containing the carbonyl group into carbon monoxide and another molecule, rather than into free radicals.[13]

However, a recent study of the photochemical decomposition of acetaldehyde throws considerable doubt on the older hypothesis that aldehydes and ketones dissociate directly into molecules; the study[14] was carried out in the temperature range 25° to 310° and at the upper limit, quantum yields as high as 300 were obtained. The chain shortens rapidly with falling temperature, and at room temperature the quantum yield of the chain reaction is only 0.03. The products of this photochemical decomposition are methane and carbon monoxide in substantially equimolecular amounts; the results of Leermakers' investigation agree quantitatively with a chain mechanism based on dissociation into radicals proposed to explain[15] the thermal decomposition of acetaldehyde. Quite recently, Norrish[16] has also adopted a free radical scheme for the photochemical dissociation of aliphatic ketones. For the lower members, such as acetone and methyl ethyl ketone, he postulates a break of the C — C chain as follows:

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[8] Norrish, *Trans. Far. Soc.*, 27, 391 (1931); Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932).

[9] The third mechanism need not be considered because it requires a great deal more energy than either of the other two.

[10] See Kirkbride and Norrish, *Trans. Far. Soc.*, 27, 404 (1931).

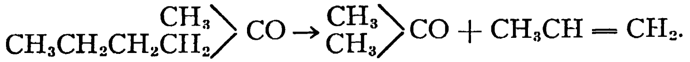
[11] See Damon and Daniels, *J. Am. Chem. Soc.*, 55, 2363 (1933).

[12] Henri, *Trans. Far. Soc.*, 25, 765 (1929); Berthelot and Gaudechon, *Compt. rend.*, 156, 68 (1913).

[13] See however, Leighton and Blacet, *J. Am. Chem. Soc.*, 55, 1766 (1933); 54, 3165 (1932).

$$CH_3COCH_3 \rightarrow CH_3CO + CH_3$$

whereas, for higher ketones, such as methyl butyl ketone, he suggests:



$$\begin{matrix} & CH_3 \\ CH_3CH_2CH_2 & CH_2 \end{matrix}\Big\rangle CO \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle CO + CH_3CH = CH_2.$$

It would be very desirable to have measurements of quantum yields for various aldehydes and ketones over a range of temperature, in order to determine definitely whether a chain phenomenon occurs.

In contrast with ketones and aldehydes, there does not seem to be any doubt that the photochemical decomposition of alkyl halides proceeds through a primary mechanism involving the separation of the halogen atom and formation of a free alkyl radical. For example, Schumacher[17] postulates a mechanism for the decomposition of ethylene iodide involving the formation of the free iodoethyl radical, CH_2ICH_2, and points out that it should be very unstable because when it loses the iodine atom the "process is coupled with the liberation of energy accompanying the formation of the C = C bond." The absorption spectra of the simple alkyl halides also indicate[18] a primary photochemical dissociation into a halogen atom and an alkyl radical. Very considerable support for this view was obtained from a comprehensive investiga-

[14] Leermakers, *J. Am. Chem. Soc.*, 56, 1537 (1934); *idem, ibid.*, 56, 1899 (1934).

[15] Rice and Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

[16] Norrish, *Trans. Far. Soc.*, 30, 103 (1924).

[17] Schumacher, *J. Am. Chem. Soc.*, 52, 3132 (1930).

[18] Herzberg and Scheibe, *Trans. Far. Soc.*, 25, 716 (1929); Iredale, *Nature*, **604**, Oct. (1930); see also Iredale, *J. Phys. Chem.*, 33, 290 (1929).

tion[19] of the photochemical oxidation of methyl iodide. It was found that when pure methyl iodide vapor at 0° is illuminated even for a long period of time, there is only slight decomposition; in the presence of oxygen, however, the rate of decomposition increases over a hundred fold and is sufficiently rapid to permit of kinetic measurements. The authors postulate a primary dissociation into $CH_3 + I$ and suggest that this behavior indicates that in the absence of oxygen the recombination reactions

$$CH_3 + I \rightarrow CH_3I \quad \text{and} \qquad 1$$

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad 2$$

predominate and are accompanied only to a minor extent by such reactions as

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad 3$$

$$CH_3 + I \rightarrow CH_2 + HI \qquad 4$$

$$CH_3 + CH_3I \rightarrow C_2H_6 + I \qquad 5$$

$$CH_3 + CH_3 \rightarrow CH_4 + CH_2 \qquad 6$$

The following reactions are thermally impossible:

$$I + CH_3I \rightarrow CH_3 + I_2 \qquad 7$$

$$I + CH_3I \rightarrow CH_2I + HI \qquad 8$$

$$I + CH_3I \rightarrow CH_2I_2 + H. \qquad 9$$

It is interesting to note that although the conditions are very favorable for reaction 5, at best it occurs to only a slight extent as compared with reactions 1 and 2.

In the presence of oxygen, the following mechanism for the oxidation of the free methyl groups was proposed:

$$CH_3 + O_2 \rightarrow HCHO + OH \qquad 10$$

$$OH + CH_3I \rightarrow CH_3OH + I. \qquad 11$$

Based on this mechanism, the observed phenomena and the observed reaction rates under different conditions could be satisfactorily explained; on the other hand a mechanism involving peroxide formation according to some such scheme as

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad 12$$

$$CH_3I + CH_3O_2 \rightarrow HCHO + CH_3OH + I \qquad 13$$

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[19] Bates and Spence, *J. Am. Chem. Soc.*, 53, 1689 (1931).

leads to the prediction that increase in total pressure at low oxygen concentration should increase the rate, whereas, experimentally, if there is any change at all it is in the opposite direction.[20]

From the relative rates of the two reactions

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad 2$$

$$CH_3 + O_2 \rightarrow HCHO + OH \qquad 10$$

it was calculated that at 0° C. the difference in the two energies of activation is $E_{10} - E_2 = 3.2$ Cal.; therefore at 0° C. reaction 2 should proceed approximately 400 times as fast as reaction 10.

Since 1925 a very considerable number of kinetic studies of the thermal decomposition of organic compounds [21] has been made. Attention has been directed mainly to the laws governing the rate of decomposition and to such questions as the rate of attainment of the Maxwellian distribution as compared with the rate of the reaction; very little attention was paid to the question of the detailed chemical mechanism and the possible production of free radicals; indeed, since so many of the decompositions follow a unimolecular law, the evidence may be said to favor a simple rearrangement or rupture into two new molecules rather than a rupture into radicals which would be likely to induce chain formation.

The situation however was quite different in a number of studies involving a reaction between a free atom and an organic compound: [21] these bimolecular metatheses have proved to offer a valuable approach to the study of free radicals. Bonhoeffer and Harteck [22] introduced various hydrocarbons in the gaseous state into atomic hydrogen, under such conditions that there were several hydrogen atoms present for each molecule of hydrocarbon. Methane was found to be different from all other hydrocarbons in that it did not react with atomic hydrogen [23] under the experimental conditions. Other hydrocarbons react readily, probably through the successive removal of the combined hydrogen atoms by the free hydrogen atoms to form molecular hydrogen; this process was found to continue until C — H radicals and finally C — C radicals were formed. Because both these radicals have a low energy of excitation they can be easily detected: the gaseous mixture flowing through the tube shows first a blue region which emits the C — H spectrum and then a green region indicative of the emission of C — C. The reactions of atomic hydrogen (produced by excited mercury atoms) with various hydrocarbons have also been studied by Taylor and his co-workers; [24] the somewhat complex processes that occur have been described qualitatively on a basis of free radical formation and interaction.

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[20] See however Bates and Lavin, *J. Am. Chem. Soc.*, 55, 81 (1933); Spence, *Trans. Far. Soc.*, 30, 141 (1934).

[21] See Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., 1931.

[22] Bonhoeffer and Harteck, *Z. physik. Chem.*, A139, 64 (1928); see also von Wartenberg and Schultze, *Z. physik. Chem.*, B2, 1 (1929).

[23] See Bates, *J. Am. Chem. Soc.*, 52, 3825 (1930).

The studies of atomic reactions of Polanyi and his co-workers [25] have thrown considerable light on the whole question of the conditions necessary for the production of free radicals. They have shown that the reaction

$$Na + CH_3I \rightarrow NaI + CH_3$$

proceeds at every collision, whereas the reaction

$$Na + CH_3Cl \rightarrow NaCl + CH_3$$

no longer proceeds at every collision but requires an activation energy of 7.5-8.8 cal. The difference in strength of different C — Cl bonds in organic molecules is strikingly shown by the activation energies of the reactions of the following compounds with sodium:

$CH_3CH_2CH_2Cl$	4.4 Cal.	$CH_3CCl=CH_2$	5.5 Cal.
$CH_3CHClCH_3$	3.3 Cal.	$CH_2ClCH=CH_2$	0.25 Cal.
$CH_3CH_2CHCl_2$	0.3 Cal.	CH_3COCH_2Cl	0.1 Cal.

From a study of the reaction between metallic sodium and alkyl halides in the presence of hydrogen, in which reaction hydrogen is used up and methane simultaneously formed, the authors conclude that the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ has an activation energy of approximately 8 Cal. However it seems doubtful whether this low value can be correct (see p. 80).

The discovery [25a] and study of the free methyl group by Paneth and Hofeditz in 1929 gave a great stimulus to the interest of organic chemists in free radicals. These authors showed that lead tetramethyl carried in a stream of pure hydrogen at pressures of 1-2 mm. can be decomposed by heating, into metallic lead and free methyl groups. The free methyl groups are carried rapidly out of the heated zone and can be made to combine with a variety of metals when these are distilled onto the walls in the form of metallic mirrors. The organometallic products thus formed were shown to consist only of the methyl derivative. The free methyl groups recombine very rapidly after leaving the furnace, and their half-life was found to be only 0.006 sec.

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[24] Taylor and Bates, *J. Am. Chem. Soc.*, 49, 2483 (1927); Taylor and Hill, *ibid.*, 51, 2922 (1929).

[25] Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930); Hartel, Meer and Polanyi, *ibid.*, **B19**, 139 (1932).

[25a] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).

Although the experimental work in this paper was very thorough and convincing, the results did not immediately meet with general acceptance. This was due, in some degree, to the failure of others to repeat the experiment.[26] A familiarity with high vacuum technique is required in order to obtain a very rapid flow of hydrogen through the tube, and also to exclude the smallest trace of oxygen, which prevents removal of the metallic mirrors. Furthermore, both the hydrogen and the lead tetramethyl must be specially purified. It was variously suggested that the effect might be due to atomic hydrogen [27] or to "hot" molecules.[28] Müller and Schultze reported that atomic hydrogen formed a lead hydride with metallic lead, and could in this way remove lead mirrors. Paneth [29] immediately answered their criticism by pointing out, quite justly, that the ability of atomic hydrogen to remove lead mirrors had nothing whatsoever to do with his experiment; he had identified the products formed by the union of the active agent with the metal of the mirror; furthermore, he had shown that zinc, which forms no volatile hydride, is readily removed by the active agent formed in the decomposition of lead tetramethyl. The argument that, because atomic hydrogen and the active agent from lead tetramethyl both cause lead mirrors to disappear, it follows that the active agent is not methyl but atomic hydrogen, is obviously quite untenable. Further work [30a] has fully supported Paneth's original position. Atomic hydrogen decolorizes many dyes and reduces copper sulfate to metallic copper; the fragments produced from lead tetramethyl and from other organic compounds show none of these effects.

The supposition that "hot molecules" cause the removal of metallic mirrors, as suggested by Burk,[28] seems to be disproven by the fact that certain organic compounds carried in a current of inert gas may be completely decomposed in the furnace [30b] yet the fragments readily remove mirrors.

[26] Paneth and Lautsch, *Ber.*, **64**, p. 2704, footnote 16 (1931).

[27] Müller and Schultze, *Z. physik. Chem.*, **B6**, 267 (1929).

[28] Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

[29] Paneth, *Z. physik. Chem.*, **B7**, 155 (1930).

[30a] Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3529 (1932).

[30b] Simons and Dull, *ibid.*, **55**, 2696 (1933).

Paneth and Lautsch[31] next prepared the free ethyl radical in a manner analogous to that used for the preparation of the free methyl group. Its properties and half life were found to be very similar to those of the methyl group; reaction of the ethyl groups with each other produces mainly butane, as compared with ethane in the case of the methyl groups. Evidence was also obtained that radicals higher than ethyl are very unstable,[31] since methyl radicals appear to be the chief product in the decomposition of lead tetra-n-propyl and lead tetra-isobutyl.

A further investigation[32] of the mechanism of the recombination of the free radicals and of their reaction with metallic mirrors showed that the nature of the transport gas (He, H_2 or N_2) has only a slight effect on the rate of recombination of the radicals; that the recombination occurs mainly on the walls and only to a slight extent in the body of the gas. Methyl and ethyl radicals adhere to a lead mirror at the first collision but only 1/1000 of the radicals striking a quartz or glass surface at room temperature are held.

In their first paper Paneth and Hofeditz had shown that the removal of mirrors could not be due to the hydrogen which was used to carry the lead tetramethyl, nor to the possible products of the decomposition such as ethylene, methane or acetylene, since none of these substances remove mirrors even when led through a very hot tube.[33] Since then Rice and his co-workers[30a] have tested many organic compounds for the Paneth effect. It has been found that a wide variety of organic compounds when heated in the range 800-1000° decompose into free radicals which readily remove mirrors. Furthermore, it was found that the vapor of the decomposing organic compound can be used to carry the free radicals; this discovery simplified the apparatus considerably since it made it unnecessary, both to supply highly purified hydrogen, and to have a powerful pumping arrangement to remove the hydrogen sufficiently quickly from the apparatus. It was also found that a condensable gas such as water vapor or carbon dioxide can be used to replace the hydrogen in the original Paneth experiment with lead tetramethyl; the effect can then be demonstrated in a very simple apparatus.

The half life of radicals produced from hydrocarbons and other aliphatic compounds varies from $1\text{-}2 \times 10^{-3}$ sec., as compared with

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[31] Paneth and Lautsch, *Ber.*, **64**, 2702 (1931).

[32] Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931).

[33] In connection with the action of ethylene see Rice and Whaley, *J. Am. Chem. Soc.*, **56**, 1311 (1934).

6×10^{-3} sec. obtained by Paneth and Hofeditz using lead tetramethyl. The identification of the radicals was accomplished by combining them with metallic mercury; the organometallic compounds thus formed react readily and quantitatively with mercuric halides to give alkyl mercuric halides which are crystalline compounds with definite melting points. A great variety of organic compounds, such as hydrocarbons, ketones, ethers, and aldehydes, produce chiefly methyl groups, which can be identified as methyl mercuric bromide. The earlier work indicated that the methyl groups were accompanied by 10-20% of some other radical, perhaps ethyl; however subsequent investigation has shown that only methyl groups escape from the furnace.[34]

It was found that fairly low pressures (of only a very few mm. at most) are essential for the detection of free radicals by the removal of metallic mirrors. When the pressure of a sample of butane was allowed to rise to 20-40 mm. even the strongest heating produced no effect on a metallic mirror; however on reducing the pressure to 1-2 mm. mirrors were again readily removed.

Paneth and his coworkers mention a number of metals (lead, antimony, zinc, cadmium and tellurium) which react readily with free radicals; presumably their oxides do not react, since with the exception of tellurium, a trace of oxygen prevents the removal of the mirror; possibly in the case of tellurium the fairly volatile oxide, TeO_2, is formed, which may sublime off leaving a clean metallic surface. Simons and Dull[35] found that the radicals from lead tetramethyl react also with carbon tetraiodide to give methyl iodide; experiments with lead tetraethyl gave the corresponding ethyl compounds. No carrier gas was used in these experiments and the lead alkyls were completely decomposed in the furnace. A detailed discussion of the reactivity of alkyl radicals is given in Chapter V.

The products formed in the thermal decomposition of lead tetramethyl and lead tetraethyl[36] under a variety of conditions have been investigated. Using lead tetramethyl and the flow method at 0.5-2 mm. pressure, ethane is the predominant product, indicating that the chief reaction is the combination of the methyl groups in the cold zone outside the furnace. In the static experiments with lead tetramethyl in the lower temperature range (250-450° C.) methane predominates; this might be expected since the conditions are right for the free methyl radicals to abstract hydrogen from the surrounding lead tetramethyl molecules. Meinert[36] found that a similar reaction occurs in the decomposition of lead tetraethyl at somewhat higher pressures; at low pressures, reactions of the ethyl radicals with themselves predominate, giving butane, ethylene, ethane and hydrogen.

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[34] Rice and Evering, *J. Am. Chem. Soc.*, **56**, 2105 (1934); Rice and Glasebrook, *ibid.*, **56**, 2472 (1934).

[35] Simons and Dull, *J. Am. Chem. Soc.*, **55**, 2696 (1933).

[36] Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1933); Meinert, *J. Am. Chem. Soc.*, **55**, 979 (1933).

We may close this chapter with a short account of the experimental proofs that have recently been given of the effect of free radicals, both in initiating chains in the decomposition of organic compounds and in inducing decomposition at temperatures far below that at which the pure compound decomposes. The first experimental proof was given by Frey[37] who heated butane containing 1% of dimethyl mercury to 525° C.; the time of heating was sufficiently long to decompose most of the dimethyl mercury but too short to decompose butane at this temperature. Under these conditions more than twenty equivalents of the butane decomposed into the usual products, plus an additional quantity of methane equivalent to the methyl groups of the dimethyl mercury. Shortly after this, Sickman and Allen[38] showed that acetaldehyde containing a few per cent of azomethane decomposes completely at 300° C., at which temperature the aldehyde alone is quite inert. Chain lengths of about 30 were obtained. Finally, Leermakers made a very careful study of the photolysis of acetaldehyde[39] and has shown it to be a chain reaction at temperatures above 80°; the kinetics of the reaction are in very good agreement with a free radical mechanism which was proposed[15] to explain the thermal decomposition of the aldehyde. Leermakers[40] has also studied the decomposition of dimethyl ether and diethyl ether by methyl radicals produced by the photochemical decomposition of some added acetone and found that in both cases chains of considerable length were induced. On the other hand methyl groups introduced into pure acetone by illumination do not initiate chains at any temperature[40] up to 400°; apparently[41] the methyl groups remove a hydrogen atom from the acetone and the resulting radicals combine to form acetonylacetone.

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[37] Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

[38] Sickman and Allen, *J. Am. Chem. Soc.*, **56**, 1251 (1934).

[39] Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

[40] Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

[41] Rice, Rodowskas and Lewis, *J. Am. Chem. Soc.*, **56**, 2497 (1934).

CHAPTER IV

PREPARATION AND IDENTIFICATION

The experimental methods used in producing free radicals depend upon passing an organic compound through a tube in a very rapid stream and at low pressures. The tube is heated at one point in order to decompose a part of the compound, and the free radicals thus formed can then be detected beyond the furnace by their action on metallic mirrors. Using relatively unstable organic compounds such as metal alkyls, azomethane, diazomethane, or ethylene oxide, the tube may be of hard glass, but in general it is necessary to use a quartz tube, which can be heated above 750° C. An inert carrier gas, such as hydrogen, nitrogen, or helium may or may not be used. When such permanent gases are used a powerful pumping system is necessary in order to pump them out of the apparatus since they are not frozen out by liquid air. In order to convey the radicals to the mirror before they will have recombined it is absolutely essential to have a very rapid flow of gas through the tube. We shall now describe in detail various experimental methods for producing free radicals.

Original Paneth Method.—Essentially, this method[1] consists of carrying pure lead tetramethyl in a current of pure hydrogen at approximately 1-2 mm. pressure through a tube at a velocity of 10-20 meters per second. Both the hydrogen and lead tetramethyl must be quite pure, particularly in regard to even the most minute quantities of sulphur and halogen compounds; further, since even a trace of oxygen will deactivate the mirror, there must be no small leaks in the apparatus. The hydrogen is prepared from zinc and sulfuric acid in a Kipp generator; after being passed through a wash bottle filled with concentrated sulfuric acid, which also serves as a bubble counter, the gas is dried by means of calcium chloride and phosphorus pentoxide. Oxygen and other foreign gases are removed by passage through a tube containing activated charcoal at liquid air temperatures. After being thus purified, the hydrogen enters the apparatus through stop-cock 1, Fig. 1. The amount of hydrogen flowing through tube A is controlled by regulating stopcocks 2, 3 and 4. The tube A contains a small quantity of lead tetramethyl and is kept at about —70° C. The lead tetramethyl should be purified by careful distillation followed by shaking for several days with freshly prepared dry silver oxide in order to remove the last traces of halogen.

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[1] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).

A quartz tube B, about 60 cm. long and 5 mm. internal diameter, is attached to tube A by means of a ground joint. After leaving tube B the gas stream either passes through stop-cock 5 and the mercury trap D to the pump, or the stop-cock 5 is kept closed and the gases are passed down the side-arm C through stop-cock 6 into a special analytical apparatus. In order to obtain the necessary high gas velocity there must be a powerful pumping system.

In this experiment a mercury-vapor pump must be used to supplement the oil pump; an ordinary two-stage glass mercury-vapor pump backed by an oil pump is adequate if the mercury vapor pump is designed for speed rather than for producing a high vacuum. However, a three- or four-stage steel mercury-vapor pump is to be preferred and is recommended for all experiments in which a permanent gas must be pumped out of the apparatus. During a run the pressure of hydrogen at the point *p* is kept at about 1-2 mm.; this should result in a stream velocity of 10-15 meters per second. In order to insure that the pumping system is adequate the pressure should be measured both at *p* and at *p′*. The vacuum is sufficient if the pressure at the latter point is not more than a few hundredths of a millimeter; lowering the pressure still further can have no appreciable effect on the rate of flow.

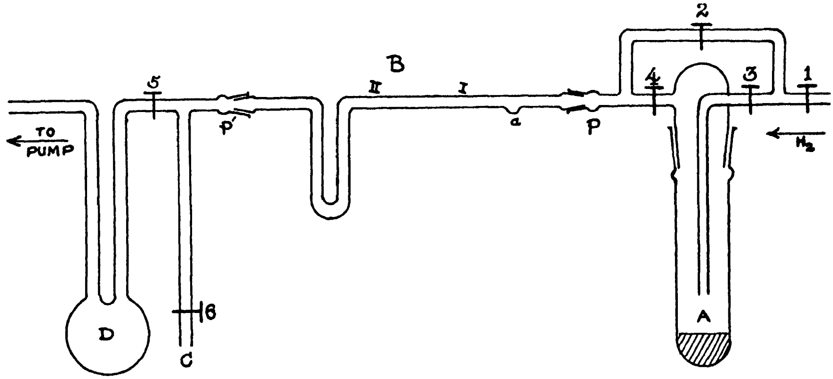

Fig. 1.—Apparatus for preparing methyl radicals from tetramethyl lead, using hydrogen as carrier gas.

A number of interesting experiments can be performed with this apparatus. For example, the formation of a mirror at one point is accompanied by the simultaneous disappearance of a second mirror further down the tube. In order to do this stop-cock 3 is opened so that the hydrogen passes through tube A and becomes saturated at —70° C. with lead tetramethyl vapor. If the quartz tube B is then heated at the point II with a Bunsen burner the lead tetramethyl decomposes and lead is deposited on the walls of the tube in the form of a mirror. If the tube B is allowed to cool at point II and is then heated at point I a new lead mirror appears at I, and in proportion as this grows the mirror at II disappears. This phenomenon can be repeated indefinitely. It is best to have the mirror which is to be removed at room temperature or a little above; if the point at which the mirror is deposited is cooled much below the adjoining parts of the quartz tube the phenomenon is definitely inhibited, possibly because the decomposition of lead tetramethyl is accompanied by the formation of minute traces of gummy substances which are then deposited on the cooled mirror, thus preventing the further reaction of the lead with the free radicals. If the smallest trace of oxygen is allowed to enter the apparatus after a mirror has been deposited the latter will not be removed by the free radicals. If, however, such a superficially oxidized mirror is heated and driven a little farther down the tube in a current of pure hydrogen, it can be readily removed by the free radicals.

This experiment may also be performed using other lead alkyls or bismuth trimethyl instead of lead tetramethyl, but the phenomenon does not occur with either zinc dimethyl or antimony trimethyl. An explanation for this is suggested on page 60.

It is not necessary to produce the mirrors by the decomposition of lead tetramethyl. A small piece of metallic lead may be introduced into the tube at *a* and carefully heated to form mirrors, or other metals, such as zinc, antimony, or bismuth, may be substituted for the lead. In all these cases the first mirror formed from a piece of metal is difficult to remove and must be driven down the tube in a stream of hydrogen; the succeeding mirrors, formed from the clean metallic surface, are readily removed.

In these early experiments the methyl groups were identified by their reaction products with either zinc or antimony. With antimony, the methyl groups form a condensate which appears to consist of two substances: one, a yellow oil which solidifies to a glowing red mass and the other a liquid, with a melting point below —20° C. These two substances were not definitely identified. However, in the case of zinc it was possible to show conclusively that zinc dimethyl is the only product formed.

Use of Condensable Gases.—It has been found possible to replace the hydrogen used in the previous experiments [2] by a condensable gas, thus simplifying the technique very considerably. In the apparatus shown in Fig. 2 water vapor can be used as carrier gas, and an ordinary oil pump is sufficient to produce the required vacuum of about 0.05 mm. Flask A contains the lead tetramethyl or other organic compound, and is maintained at a temperature such that the vapor pressure is in the range 5-50 mm. A short length of capillary tubing is attached to tube E by means of rubber tubing, so that the flow of the vapor from flask A may be more easily regulated by stop-cock 1. The tube B contains water at 0° C.; during an experiment lead tetramethyl vapor is allowed to bubble through the water. The other parts of the apparatus are similar to those used in Paneth's original experiment.

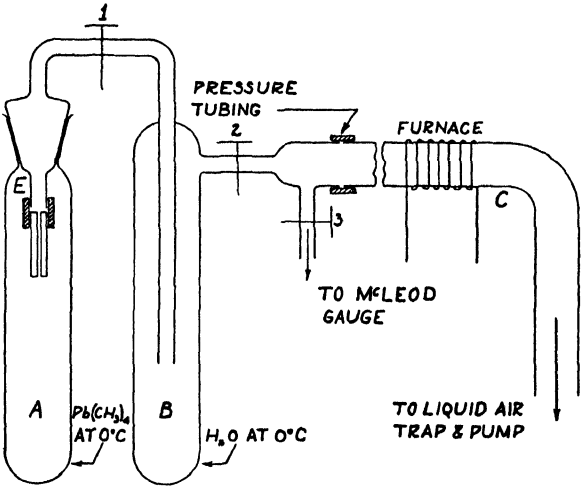

Fig. 2.—Apparatus for preparing methyl radicals from tetramethyl lead, using water vapor as carrier gas.

The radicals may also be carried in carbon dioxide, in which case the lead tetramethyl is kept in tube B, at a temperature of about —70° and solid CO_2 is kept in flask A which is maintained at about —100°.

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[2] Rice, Johnston and Evering, *J. Am. Chem. Soc.*, 54, 3529 (1932).

It is possible to simplify the apparatus still further by using a solution of lead tetramethyl in an organic solvent such as heptane or acetone. In this case no other transport gas is required and tube B can be eliminated; the temperature of A is so adjusted that the vapor pressure of the organic compound as it enters the furnace is 1-2 mm.

The simplest apparatus yet evolved is shown in Fig. 3. This is the apparatus referred to in all of the following discussions. A 1% solution of lead tetramethyl in acetone or heptane is put into tube A. The stop-cock 1 is opened and the apparatus is evacuated. This automatically removes all oxygen from the apparatus and after one or two minutes the stop-cock is again closed. The furnace is then heated to 500-600° and a metallic mirror is formed by heating a piece of metal which has previously been introduced into the quartz tube at C. The mirror is cooled with water, the stop-cock 1 is opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror. Frequently the first mirror is either not removed or removed only with difficulty because of surface impurities; it is best therefore to heat this and drive it down the tube while the current of gas is flowing. The stop-cock may then be closed and a new, clean, mirror formed.

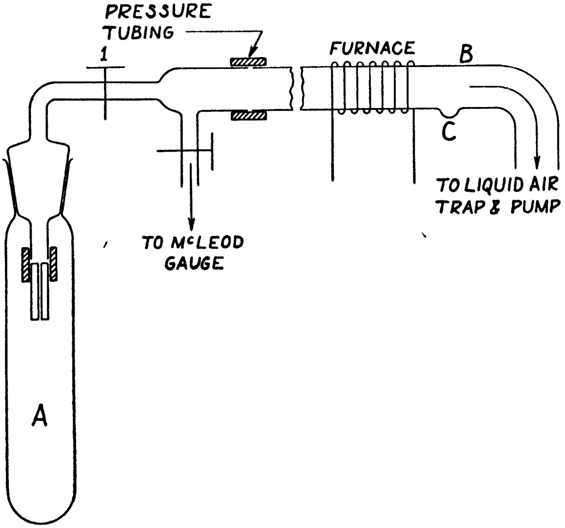

Fig. 3.—Apparatus for preparing free radicals by the thermal decomposition of organic compounds.

Free Radicals from Non-Metallic Organic Compounds.—Numerous classes of organic compounds, such as hydrocarbons, ketones, ethers, etc., can be decomposed into free radicals in the apparatus shown in Fig. 3. The vapor of the material itself is used as transport gas for the free radicals; the only modification in method, from that used when an organo-metallic compound is decomposed, is that the furnace must be heated to a higher temperature, usually in the range 750-950° C. When using this apparatus for the decomposition of non-metallic compounds, the flask A containing the compound, is evacuated for a few minutes so as to remove all air from the apparatus. The temperature of the flask and the size of the capillary are so adjusted that the vapor pressure at the inlet end of the quartz tube B is in the range 0.5 to 2 mm. A good oil pump, capable of producing a vacuum of 0.05 mm., is sufficient, although an auxiliary mercury vapor pump is desirable on account of the higher speed of evacuation.

A great variety of organic compounds, such as hydrocarbons, alcohols, ketones, acids, ethers, aldehydes, and amines, have been found to remove mirrors of many different metals, such as lead, antimony, and zinc, when passed through a furnace heated to some point above the decomposition temperature of the compound. Some compounds, such as ethylene oxide, azomethane, and azoisopropane are relatively less stable, and in some cases decompose at temperatures as low as 450°. On the other hand, ethylene is a curious exception, in that it is extremely stable, showing no sign of decomposition even at the softening point of silica.

Preparation of the Methylene Radical.—It has not been possible as yet to prepare the methylene radical by heating organic compounds to a high temperature; in general, under such conditions only methyl groups are formed, and these seem to be extremely stable and not at all easily decomposed into methylene groups and atomic hydrogen. Therefore it seemed desirable to use some compound containing the CH_2 group linked to some other bivalent radical. Because of its great stability, ketene, $CH_2{=}CO$, is not a very suitable source for preparing CH_2 groups; on the other hand, diazomethane, $CH_2{=}N{\equiv}N$, decomposes easily and provides a convenient source of this radical.[8] The diazomethane is best kept in solution in a non-volatile solvent such as dibutylphthalate; such a solution may be preserved for many weeks at —80° and used when required. In an actual experiment a small quantity of the dibutylphthalate-diazomethane solution is added to flask

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[8] Rice and Glasebrook, *J. Am. Chem. Soc.*, 55, 4329 (1933).

A, Fig. 3, which contains also a low boiling organic compound such as butane or ether to serve as carrier gas. The quantities are so arranged that the solution contains 1-2% of diazomethane. When the diazomethane-butane mixture is passed through the furnace, very curious phenomena are observed. At temperatures above 700° C., when the ether is also decomposed, mirrors of zinc, cadmium, lead, antimony, and tellurium are all readily removed. As the temperature of the furnace is lowered we come to a point at about 600°, at which the zinc, cadmium, and lead mirrors are not affected, but antimony and tellurium mirrors are readily removed. Finally we come to a second point at about 350°, below which there is no removal of any mirrors. It has been shown[4] that the methylene radical is formed in the decomposition of diazomethane under these conditions in the range 350-600° At higher temperatures the methylene groups from the diazomethane attack the butane or ether used as carrier gas and form methyl radicals.

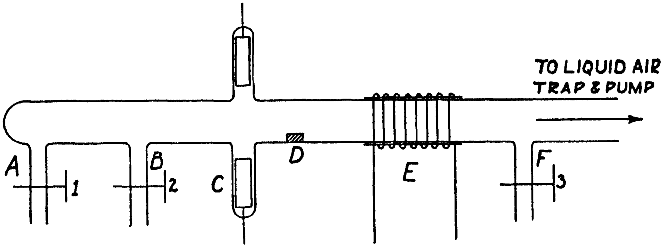

Fig. 4.—Apparatus for preparing free radicals by the electrical decomposition of organic compounds.

Production of Free Radicals in a Discharge Tube.—A number of organic compounds, such as butane, heptane, acetone, and ethyl alcohol, when passed through a discharge tube at low pressures are decomposed with the production of alkyl radicals.[5] The essential features of the apparatus are shown in Fig. 4. A flask containing the organic liquid is connected with the discharge tube C through a length of capillary tubing and stop-cock 1. The flask is kept at a temperature such that the vapor pressure of the compound at the discharge tube is in the range 3-0.5 mm. The discharge tube is equipped with electrodes of sheet aluminium; these are connected with a 500-watt transformer which furnishes 1000 volts. The entire apparatus is of pyrex, and is evacuated by a mercury-vapor pump backed by an oil pump. Small pieces of metal D can be introduced at different distances from the discharge tube, and by cautious heating, mirrors can be distilled onto the walls. Numerous organic compounds will remove antimony and lead mirrors in such an apparatus, but curiously enough neither zinc nor cadmium mirrors are affected. The effect does not seem to be due to atomic hydrogen since tests with copper oxide and with several dyestuffs were negative. An attempt has been made to identify the fragments by combining them with mercury, according to the method described in the following section. It seems clear that some kind of unstable mercury alkyls are formed, and in the case of acetone, methyl mercuric bromide was isolated.

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[4] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).

[5] Rice and Whaley, *J. Am. Chem. Soc.*, **56**, 1311 (1934).

One result of these experiments is interesting. Even on heating to 1000° ethylene does not remove mirrors; however, when passed through a discharge tube it readily removes antimony and slowly removes lead mirrors; an attempt to identify the fragments by combining them with mercury was unsuccessful.

Reaction between Sodium Vapor and Alkyl Halides.—These reactions have been studied in considerable detail by Polanyi and his co-workers and have recently[6] been adapted for the preparation of free radicals. In this method sodium vapor, at a pressure of about 10^{-3} mm., is carried in a current of permanent gas at a pressure of 4-5 mm.; the gaseous mixture is led through a nozzle into a reaction zone I containing an alkyl bromide at pressures of a few hundredths of a mm. The reaction that occurs can be represented by the equation: $Na + RBr \rightarrow NaBr + R$; this reaction has an activation energy varying from 1.0 to 2.5 Cal., depending on the alkyl halide used. The speed of the reaction was measured by observing the disappearance of the sodium vapor by means of a sodium resonance lamp. Care was taken to see that the primary reaction went fully to completion before the gas mixture left zone I; the gas stream carrying the free radicals R left zone I through a nozzle and entered zone II, where some reagent could be added to enable the free radical R to be identified. Iodine proved to be very suitable for this purpose and in several experiments the iodide formed was identified and estimated. The free radicals methyl and ethyl were formed in this way and could be detected at a considerable distance

[6] Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930); Polanyi and Style, *Naturwiss.*, **20**, 401 (1932); Hartel, *Trans. Far. Soc.*, **30**, 187 (1934); Horn, Polanyi, and Style, *ibid.*, **30**, 189 (1934).

from their source. Only about 10% of the alkyl halide that reacted was recovered as the iodide formed from the free radicals. An approximate calculation indicated that the free radicals disappear through a bimolecular reaction which occurs at every collision between two radicals. Similar experiments were performed in which the sodium was carried in a stream of hydrogen, and chlorine was added in zone II; in this case the free radicals initiated a chain reaction between the hydrogen and chlorine, and the results obtained in this case agreed with those obtained when sodium was used.

Identification of Free Radicals.—Paneth and Hofeditz[1] identified the free methyl group produced in their experiments by combining it with zinc; zinc dimethyl was identified by its melting and boiling points, and from its spontaneous combustion in air with the separation of zinc oxide. They also showed quite clearly that antimony alkyls were formed when antimony mirrors were removed, but since there was a mixture, a satisfactory identification was not possible with the small quantity available. Paneth and Lautsch[6a] identified the free ethyl group prepared from lead tetraethyl in a similar manner. They obtained final identification through the formation of the compound $C_2H_5OOZnC_2H_5$ as the result of the partial oxidation of their product. This compound precipitates as a white powder which can be readily hydrolyzed and the ethyl alcohol formed identified by the iodoform test.

Recently the action of free radicals on metallic sodium and on carbon tetraiodide has been used for identification purposes.[7] In these experiments lead tetramethyl, without any carrier gas, was passed through a furnace at a temperature of about 900° C. and a pressure of a few hundredths of a millimeter. In the first experiment the fragments were allowed to come in contact with sodium, and the mixture of sodium and sodium alkyl was treated with alcohol and the gases analyzed. Methane was the only hydrocarbon produced in sufficient quantities to be identified. Similarly, when lead tetraethyl was used, ethane was the only hydrocarbon found.

In another experiment using lead tetramethyl as source material the alkyl iodides formed by reaction of the fragments with carbon tetraiodide were combined with quinoline. The melting point of the resulting product was identical with that of a synthetic sample of quinoline methiodide, and a mixed melting point determination confirmed the identity. Similar experiments with lead tetraethyl served to identify the ethyl radical. It seems clear from these experiments that the methyl group does not easily decompose into the methylene radical and atomic hydrogen, and similarly, that the ethyl group does not decompose to any significant extent into the ethylidene radical and atomic hydrogen; if either of these decompositions had occurred methylene iodide and 1, 1–diiodoethane would necessarily have been produced.

[6a] Paneth and Lautsch, *Ber.*, 64, 2702 (1931).

[7] Simons and Dull, *J. Am. Chem. Soc.*, 55, 2696 (1933).

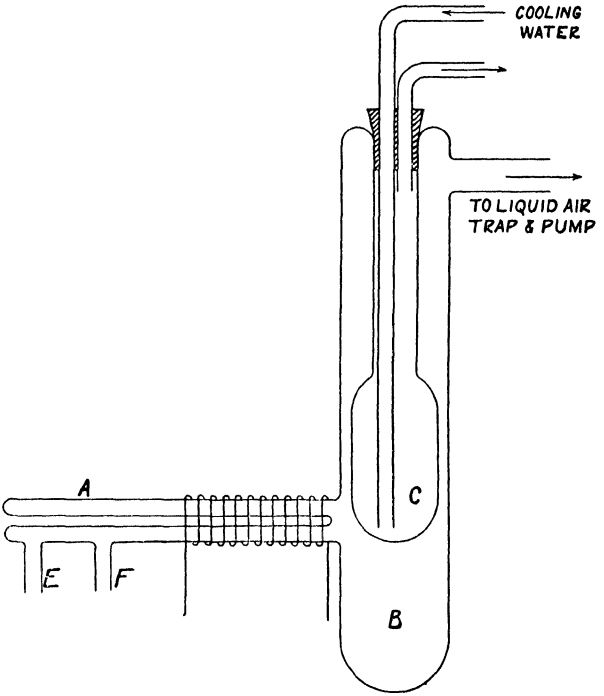

Fig. 5.—Apparatus for the identification of free radicals by combination with mercury.

In the ordinary pyrogenic decomposition of organic compounds, there is always a large excess of the undecomposed original compound mixed with the decomposition products. For this reason it is especially desirable to find a metal which combines readily with the free radicals and from which one can easily prepare stable crystalline derivatives having definite melting points and, if possible, containing only one alkyl group in the molecule. Mercury seems to be almost unique in having all of these properties. The mercury dialkyls are very volatile and extremely poisonous compounds, but they react quantitatively with mercuric chloride and mercuric bromide, producing the corresponding alkyl mercuric halides; these compounds have nearly all been studied and are well-defined crystalline compounds with definite melting points.[8] The apparatus which has been found most satisfactory is shown in Fig. 5.

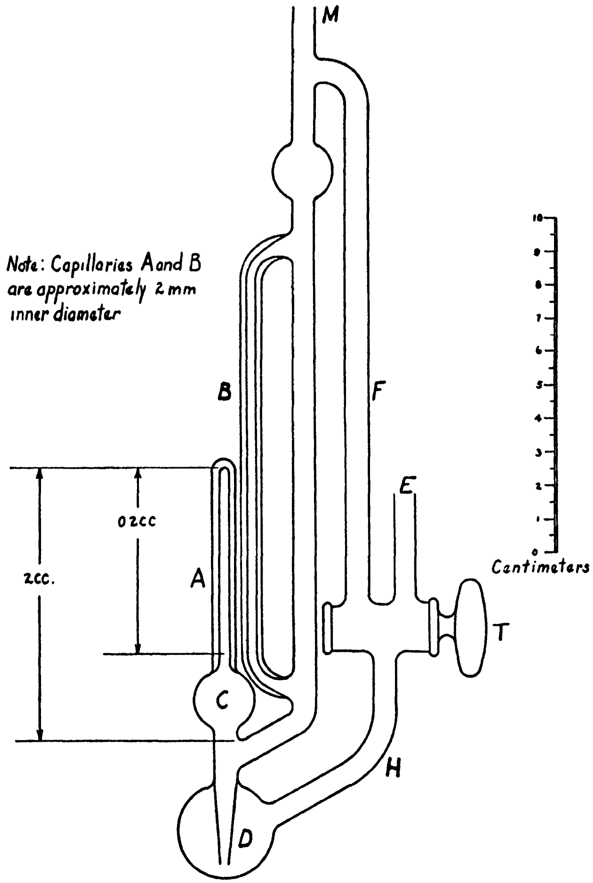
M
Note: Capillaries A and B are approximately 2 mm inner diameter
B
F
E
0.2cc
2cc.
A
C
D
H
T
10
9
8
7
6
5
4
3
2
1
0
Centimeters

FIG. 6.—McLeod gauge.

The organic compound is kept in a tube which is not shown in the sketch but is similar to tube A, Fig. 3. This tube is connected through a stop-cock with side-arm E. The second side-arm F connects with a McLeod gauge. The side-arm A is further fitted with a thin quartz tube of 0.2 mm. inside diameter to accommodate a thermocouple. The temperature of the organic compound is so arranged that a pressure of about 1 mm. is maintained at the entrance to side-arm A; the latter can be heated by means of an electric furnace about 10 cm. long to 800-1000° C. Fig. 6 is a sketch of a small McLeod gauge which we have found very convenient for measuring pressures in the range 0.1-5 mm.

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[8] Whitmore, *Organic Compounds of Mercury*, Chemical Catalog Co., 1921.

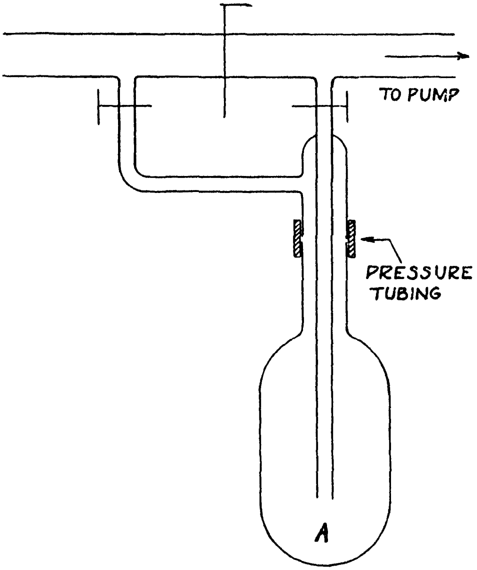

FIG. 7.—Apparatus for preparing alkyl mercuric halides.

After the bulb D is filled with mercury the gauge is attached to the apparatus at M by means of a short piece of pressure tubing. Since the complete guage is only ten to twelve inches long it does not require any stand and can simply be suspended from its point of attachment to the apparatus. The dimensions of the bulb C and the capillary are so arranged that the pressure is multiplied 10 to 20 times.

The quartz tube B (Fig. 5) contains a few cc. of mercury; when this is heated it distils and condenses on the water-cooled tube C. This apparatus can be run continuously for several hours and requires no attention beyond occasional renewal of the liquid air. The yields of mercury alkyl depend, naturally, on the extent to which the compound is decomposed; one experiment decomposing butane at 1000° C. yielded a mixture of alkyl mercuric bromides at the rate of 1 gram per hour. At the end of a run the contents of the liquid air trap are allowed to warm up to room temperature and the mercury alkyls, undecomposed organic compound, and any other volatile substances are distilled off in the apparatus shown in Fig. 7. This apparatus can very conveniently be incorporated between the liquid air trap and the mercury vapor pump (see Fig. 5). The flask A, Fig. 7, contains an excess of saturated alcoholic mercuric bromide; after the contents of the liquid air trap have distilled over into this, the flask is allowed to warm up to room temperature to permit the reaction between the mercuric bromide and the mercury alkyls to occur. Care must be taken that organic compounds containing inorganic mercury salts or finely divided mercury are not brought above room temperature, in order to avoid all possibility of the formation of organometallic compounds. Frequent tests have shown that there is no danger of reaction between inorganic mercury

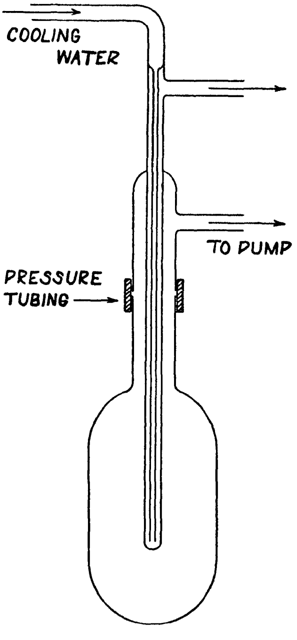

FIG. 8.—Apparatus for subliming alkyl mercuric halides

salts and organic compounds if all the operations involved are conducted at room temperature or lower.[9]

After the reaction between the mercury alkyls and the mercuric bromide is completed, which requires a few minutes, the solution is evaporated to dryness at room temperature or lower under diminished pressure. The alkyl mercuric bromides can then be separated from the excess of mercuric bromide by sublimation in the apparatus shown in Fig. 8. The first fraction obtained is usually pure methyl mercuric bromide, regardless of what organic compound has been used as a source of the radicals. Later fractions consist of mixtures of methyl mercuric bromide and one or more less volatile derivatives. These latter have not yet been identified with certainty, although X-ray photographs indicate that under certain conditions ethyl mercuric bromide is present. Fig. 9 shows a comparison of the X-ray data obtained from various pure substances and from the products of certain experiments.[9a]

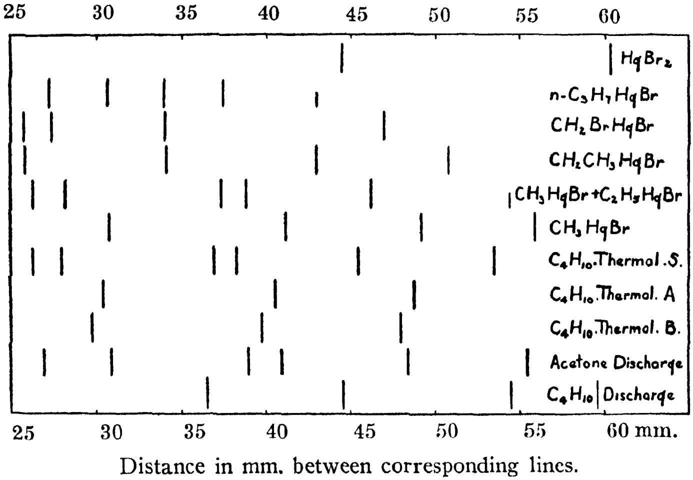

FIG. 9.—X-ray spectra of organo compounds of mercury.

More recent work[10] has shown that the fragments produced in the thermal decomposition of propane and butane react with mercury to give upwards of 95% dimethyl mercury. Ethyl groups were tested for by a method developed by Willstätter and Utzinger[11] which depends on the relative insolubility of tetramethyl ammonium iodide in such solvents as water, acetone, chloroform, and absolute alcohol, in all of which trimethyl ethyl ammonium iodide dissolves freely. No trimethyl ethyl ammonium iodide was found when the mercury dialkyls formed in the thermal decomposition of either propane or butane were converted into alkyl iodides and these in turn reacted with trimethyl amine to form the quaternary iodides. The difficulties in previous work were found to have been caused partly by the presence of a small amount of mercuric bromide which sublimes with the alkyl mercuric bromide, and partly by the formation of a small quantity of some very unstable alkyl mercurous compound, which decomposes in a few hours even at —80° ; this may possibly be the compound $CH_3HgHgCH_3$. The reaction of this compound with mercuric bromide might be expected to lead to the formation of mercurous bromide which was actually found to be present with the residue of mercuric bromide after sublimation of the alkyl mercuric bromides.

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[9] This may not be true with very reactive organic compounds such as diazomethane; see Hellerman and Newman, *J. Am. Chem. Soc.*, 54, 2859 (1932).

[9a] See Rice and Whaley, *J. Am. Chem. Soc.*, 56, 1311 (1934).

[10] Rice and Evering, *J. Am. Chem. Soc.*, 56, 2105 (1934).

An improved technique[11a] for identifying radicals through their alkyl mercury compounds consists in adding the contents of the liquid air trap after an experiment, to an excess of pure ether and filtering from the suspended mercury. An excess of an alcoholic solution of mercuric bromide is then added, and the solution is evaporated to dryness under a partial vacuum. During all these operations the solution is kept below room temperature. The residual solid, consisting of the alkyl mercuric bromides with the excess of mercuric bromide, is steam-distilled. This effects a complete separation of the alkyl mercuric bromides, which are readily volatile with steam, from the excess of mercuric bromide, which is quite non-volatile. The alkyl mercuric bromides are filtered and dried in a vacuum, and can then be identified.

Metallic tellurium[12] has also been found to be an excellent agent for the identification of methyl groups. Paneth and Lautsch[13] had already observed some time ago that mirrors of this metal are removed by free radicals and further that they are not deactivated by traces of oxygen; these authors however did not examine the products of reaction between the tellurium and the radicals. When the fragments obtained in the thermal decomposition of butane, acetone, or diethyl ether are brought into contact with metallic tellurium, a deep red liquid, dimethyl ditelluride, $CH_3TeTeCH_3$, is the only product. This compound has a low vapor pressure at room temperature and can usually be easily separated from the excess of the undecomposed organic compound used to produce the free radicals; further, it is stable in the air, and melts sharply at —19.5°. When identifying methyl groups in this manner, it is convenient to insert the special trap shown in Fig. 10 between the tellurium mirror and the usual liquid air trap. The dimethyl ditelluride condenses as a flaming red solid on the inner tube, A, which is filled with dry ice. When sufficient material has collected, air is admitted to the apparatus, a thermometer is placed in tube A, which is allowed to warm up gradually, and the temperature at which the red compound melts is noted. This method is very convenient when the organic compound used to produce the free radicals has at least an appreciable vapor pressure at —80°.

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[11] Willstätter and Utzinger, *Ann.*, **382**, 148 (1911).

[11a] Rice and Rodowskas, *J. Am. Chem. Soc.*, March, 1935.

[12] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 2472 (1934).

[13] Paneth and Lautsch, *Ber.*, **64**, 2708 (1931).

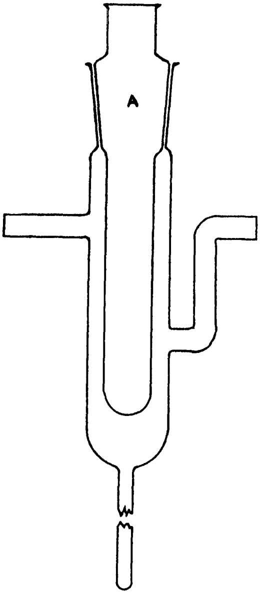

Fig. 10.—Trap for collecting dimethylditelluride.

Identification of the Methylene Radical.—Since this radical is even more specific than the alkyl radicals in its tendency to combine with only certain of the metals,[14] it can easily be distinguished from the univalent radicals: it removes tellurium, antimony, selenium and arsenic mirrors readily but does not attack those of zinc, cadmium, bismuth, thallium or lead, all of which are removed readily by methyl groups. This effect is shown in a very striking manner in Figs. 11 and 12.

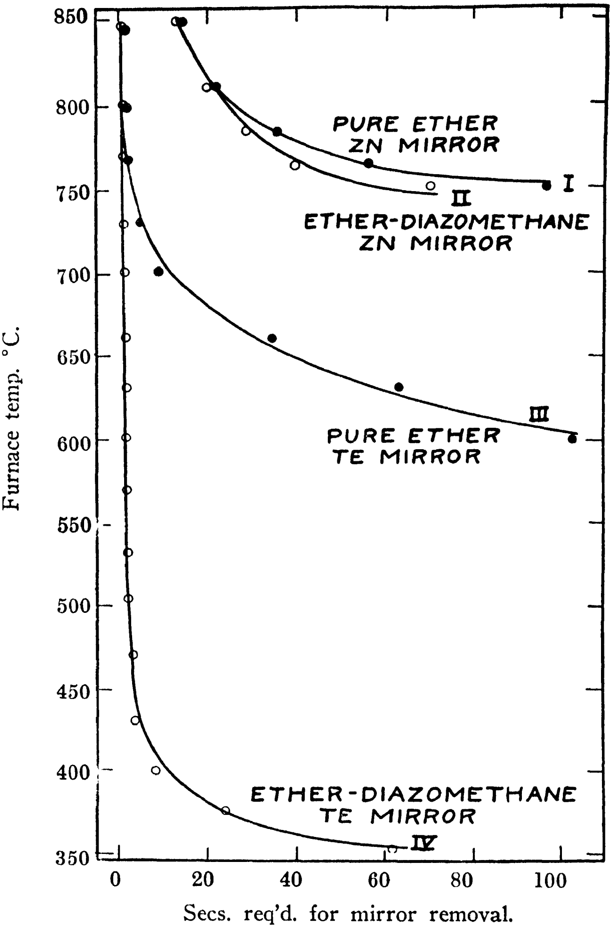

Fig. 11.—Comparison of the reaction of methyl and methylene radicals with metals.

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[14] Rice and Glasebrook, *J. Am. Chem. Soc.*, (a) **55**, 4329 (1933); (b) **56**, 2381 (1934).

The experiments on which these figures are based were performed as follows: pure ether and ether containing a little diazomethane were passed through a furnace and over standard mirrors of various metals;

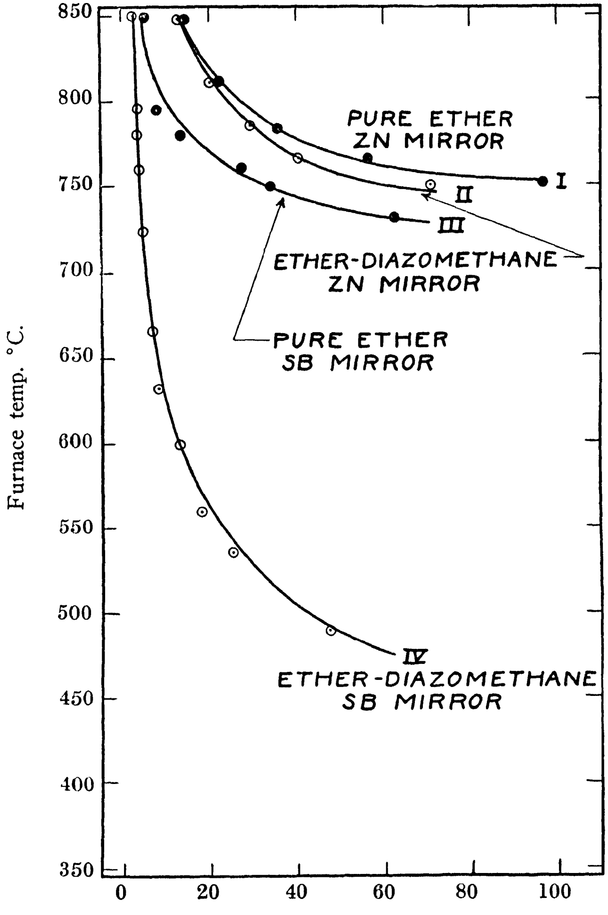

Fig. 12.—Comparison of the reaction of methyl and methylene radicals with metals.

the time of removal of the mirror was plotted against the furnace temperature. It will be seen (Fig. 11) that the two curves practically coincide when metallic zinc is the metal used. On the other hand, when tellurium is used, the ether-diazomethane mixture removes mirrors at a much lower temperature than does pure ether alone, proving the presence of some additional fragment in the mixture. Similar results are shown in Fig. 12 for which zinc and antimony were used as standard mirrors.

The conclusive identification of the fragment[14a] as the methylene radical was accomplished by isolating and analysing the product of its combination with tellurium. When methylene groups are passed over a tellurium mirror, a dark red solid condenses on the wall of the tube immediately beyond the mirror. This substance is so involatile that it cannot be driven down the tube without decomposition, but it can be sublimed onto a cooled small concentric tube, which can then be removed. Analysis shows the compound to have the empirical formula HCHTe: that is, it is telluroformaldehyde, though probably in a highly polymerised state. This compound is insoluble in the common organic solvents and decomposes if heated much above 100°. Thus we have a very convenient method of identifying methylene groups even in the presence of methyl radicals, since the product formed by the methyl groups, dimethyl ditelluride, is fairly volatile and passes over into the liquid air trap.

Identification of Hydrogen Atoms.—Since hydrogen atoms may well be present with the other fragments produced in the thermal decomposition of organic compounds, it becomes necessary to consider the reaction of hydrogen atoms with metallic mirrors.[15] Germanium, tin, arsenic, antimony and tellurium mirrors are all readily removed by atomic hydrogen but are not, of course, affected by molecular hydrogen. On the other hand, atomic hydrogen does not remove either lead or bismuth mirrors, so that we have here a convenient test to distinguish between alkyl radicals, which combine readily with both lead and bismuth,[16] and hydrogen atoms, which do not combine with these metals.

[14a] Apparently it does not react with acids to form esters according to the equation $RCOOH + CH_2 \rightarrow RCOOCH_3$ because an attempt to make it react with benzoic acid was not successful. (Paneth, *Trans. Far. Soc.*, **30**, 89 (1934).)

[15] Pearson, Robinson and Stoddart, *Proc. Roy. Soc.*, **A142**, 275 (1933).

[16] However the heat given out by the combination of hydrogen atoms with each other to form molecular hydrogen, on the surface of a bismuth mirror frequently causes distillation of the mirror and formation of a new mirror further down the tube, so that this is a possible source of error which must be avoided in such a test.

CHAPTER V

PROPERTIES AND REACTIONS

The most striking property of free radicals is their short life; if they are formed according to one of the methods described in the foregoing chapter they usually move through the tube at a rate of approximately 10^3 cm. per sec.; a light metallic mirror placed 1 cm. from the end of the furnace may be removed in a second or two but it will require many minutes to remove an identical mirror at a distance of 20 or 30 cms.

The first measurements of the half life were made by Paneth and Hofeditz.[1] Methyl groups were prepared by decomposing lead tetramethyl in a current of hydrogen and the time of disappearance of a standard antimony mirror was used as a measure of the concentration of the radicals. Mirrors were deposited at different measured distances from the furnace under identical conditions; the times of disappearance give a relative measure of the concentration of the radicals at the different points. It is also necessary to know the rate of flow of hydrogen through the tube. This can be measured by allowing the hydrogen to enter the apparatus through a bubbler which has previously been calibrated by allowing the bubbles to enter an evacuated flask and measuring the increase of pressure after a known interval of time. It is further necessary to know the pressure in the apparatus in the region from the end of the furnace to the standard mirrors. The values obtained in one experiment in which hydrogen was passed through the tube at 14 m. per sec. are shown in Table I.

TABLE I

Rate of Disappearance of Free Methyl Radicals in Hydrogen

d	$t \times 10^3$	t_m (secs.)
4	2.9	4
8	5.7	11
13	9.3	20
18	12.9	25
22	15.7	45
28	20.0	70
33	23.6	100
37	26.4	150

d is the distance from the center of the mirror to the furnace; t is the time required for the radicals to pass from the furnace to the standard mirror; t_m is the time of disappearance of a standard mirror. By plotting t against $1/t_m$ a curve is obtained showing the fall in concentration of the free radicals with time. It turns out that curves obtained in this way all follow the law of a unimolecular reaction and the half life of the methyl radical is found to be about 0.006 sec. This is a very short life compared with that of atomic hydrogen, which has been estimated very approximately to have a half life of about 0.1 sec. under similar conditions.

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[1] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).

In a later paper Paneth and Lautsch [2] describe experiments to determine to what extent the rate of disappearance of the radicals in quartz and glass tubes is dependent on the pressure and nature of the transport gas, the diameter of the tube and the concentration of the radicals. The measurements were carried out according to the former procedure except that a correction was introduced to take account of the pressure gradient from the furnace to the mirrors. In the first experiment it was shown that the half life period of the ethyl group is very nearly the same as that of the methyl group. Results obtained using quartz tubes did not differ materially from those using ordinary potash glass, nor did either the concentration of the radical or the pressure of the transport gas over the range 1-4 mm. have any marked effect. Since there was the possibility that the free radicals might react with hydrogen, the results obtained by replacing the hydrogen as transport gas with nitrogen, helium and helium-neon mixtures are of interest. The half life measurements using these gases are found to be approximately the same as those made with hydrogen as transport gas; therefore we may conclude that such reactions as $CH_3 + H_2 \rightarrow CH_4 + H$ do not occur to any appreciable extent under these conditions. However, the diameter of the tube is found to affect the half life of the radicals very considerably; a tube about 0.5 cm. diam. and a tube 1.5 cm. diam. give values for the half life of 5×10^{-3} and 15×10^{-3}, respectively. We must assume therefore that the disappearance of the free radicals is primarily a wall reaction [3] since collisions in the gas phase are too few to account for the observed rate of disappearance of the radicals.

Slightly different results are obtained when the permanent gases used to carry the lead tetramethyl in these experiments are replaced by an organic vapor such as acetone.[4] Table II shows the results obtained using a quartz tube 0.4 cm. in diameter with a pressure of 0.22 mm. of acetone at the standard mirror.

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[2] Paneth and Lautsch, *Ber.*, **64**, 2708 (1931).

[3] See also Paneth and Herzfeld, *Z. Elektrochem.*, 37, 577 (1931).

[4] Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3529 (1932).

TABLE II

RATE OF DISAPPEARANCE OF FREE METHYL GROUPS FROM LEAD TETRAMETHYL
Using acetone as transport gas. 1% lead tetramethyl in acetone.

d, cm.	34	32	30	28	26	24	22	20
$\Delta t \times 10^4$, sec. ...	74.6	68.5	63.0	57.3	52.0	47.0	42.2	37.6
t_m, sec.	183	163	132	88	86	68	47	32

d is distance from furnace to standard mirror; Δt, time taken to travel from furnace to standard mirror; t_m, time required to remove standard mirror.

The constants calculated according to a first order equation show considerable drift, so that the half life varies from 1–2 × 10^{-3} seconds, as compared with a value of 6 × 10^{-3} seconds obtained by Paneth and Hofeditz using a permanent gas as carrier. There is somewhat better, but still not very good, agreement using a second order equation.

The life of free radicals formed by heating various organic compounds in the range 800-1000° C. has also been measured. Radicals produced by heating heptane, acetone, azo-isopropane, and diethyl ether gave results very similar to those obtained when lead tetramethyl was decomposed in a current of acetone; the half life of the fragments varied from 0.5–3.0 × 10^{-3} seconds, when calculated according to a unimolecular law; the rate of disappearance, however, did not follow either a first order or second order equation very exactly.

Reactions at Solid Surfaces.—Paneth and Lautsch [2] showed that the rate of combination of free radicals is practically the same in quartz tubes and in tubes of potash glass. They also showed that a glass plate 30 cm. long by 0.3 cm. broad has the same effect whether it is of smooth glass or of glass etched with hydrofluoric acid; an iron plate of the same size has the same effect as the glass plates. The authors comment on this phenomenon in view of the active catalytic effect of iron on the recombination of atomic hydrogen.[5] Other experiments [4] along these lines have also been performed. A platinum-rhodium thermocouple, sensitive to 0.5°, showed no rise in temperature when placed in a current of hydrogen carrying the free methyl groups; a lead mirror was readily removed after the gas had passed over the thermocouple, thus affording proof of the presence of free methyl groups. In other experiments coils of wire consisting of about 20 turns of 0.2 mm. diameter wire were inserted in the tube beyond the furnace. Three experiments were performed using coils of copper, iron, and nickel wire respectively. In each case there was no perceptible effect on the methyl groups; that is, lead mirrors were removed apparently just as easily with the coil in place as in the control experiments. Moreover, heating the wires up to about 300° was also without effect.

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[5] Incidentally this experiment with the iron plate provides conclusive evidence that the removal of mirrors is not caused by atomic hydrogen.

In another experiment a heavy lead mirror was deposited for about 3 cm. along the tube; free methyl groups could not pass this in the cold, since they combined with the lead to form lead tetramethyl; but on heating the mirror to about 200° the free methyl groups apparently pass through unchanged, since they readily remove cold lead mirrors further down the tube. Paneth and Herzfeld[3] describe some experiments to determine how wide a lead mirror must be in order to stop completely the passage of the free radicals; it was found that such a guard mirror of 10 mm. width was sufficient to prevent the passing of any free radicals, whereas a mirror of only 5 mm. width allowed considerable attack on a mirror placed further down the tube. Calculations based on these measurements show that a free radical is held by the mirror on the first collision.

In their original paper Paneth and Hofeditz[1] mention the following substances as being subject to attack by free methyl radicals: lead, antimony, zinc, bismuth, and sulfur. Paneth and Lautsch[2] also mention tellurium; this metal has special advantages in that it appears to be the only metal which is not completely inactivated by a trace of oxygen. We may therefore infer from the earlier work that free radicals do not combine with metallic oxides but react readily with certain metals, most of which seem to occur in the sub-groups of the periodic table. Further work[6] has shown that the free radicals react with a wide variety of metals. They have been found to react readily with: lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium. The following metals gave negative results: magnesium, copper, silver, gold, and cerium. In general, therefore, it may be said that, with some exceptions, the metals of the sub-groups in the periodic table, the alkali metals, and some of the alkaline earth metals, react with free radicals. During this same work a number of compounds were tested for reaction with free radicals; however only one compound, namely arsenic tri-iodide, was found to react. Among the compounds tested were: mercurous chloride, mercurous bromide, lead chloride, lead iodide, and stannous iodide. In most cases a little of the compound was distilled onto the walls of the tube and a visual observation sufficed to determine whether the free radicals had any effect. Recently carbon tetraiodide[7] has been reported to react with methyl and ethyl groups, forming methyl and ethyl iodides respectively. In another series of experiments[6] no effect was found on such dyes as indigo or eosin, so that we may assume that free methyl groups have no action on these

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[6] Unpublished work by F. O. Rice, W. R. Johnston, B. L. Evering and A. L. Glasebrook.

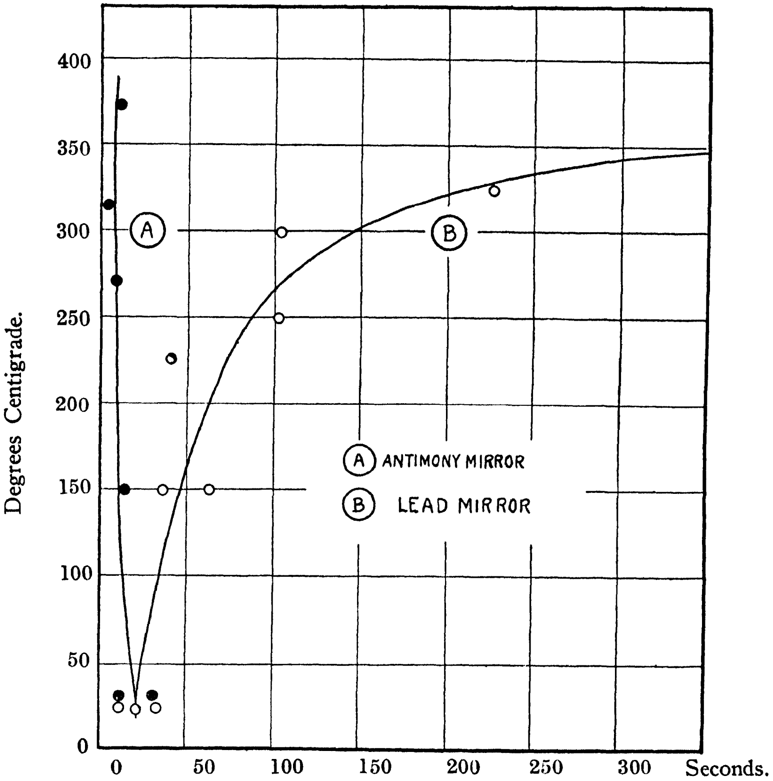

FIG. 13.—Relation between temperature of standard mirrors and time of removal by free radicals.

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[7] Simons and Dull, *J. Am. Chem. Soc.*, **55**, 2696 (1933).

substances.[8] We may conclude then from these experiments that, in general, free radicals do not react with compounds. It is possible that iodides may constitute an exception in the case of those compounds in which the iodine is weakly bound to an element of comparatively small atomic volume. Possibly this failure of methyl groups to react with compounds may be traced to a surface effect, due to which the metallic atoms are removed by the radicals, leaving the surface covered by the other part of the molecule, which may be much less subject to attack. If this is the case reaction may be expected to occur at liquid surfaces.

It is interesting to note that cooling a small section of the tube to liquid air temperatures completely prohibits all passage of the radicals;[1] apparently, under these conditions the radicals are held on the cold surface at the first collision and combine to form ethane or butane. A few experiments in which the tube was heated have also been reported;[2] the effect of this is first to increase, and then to decrease, the life of the radicals; however it should be noted[8a] in this connection that heating the methyl groups in a current of hydrogen should cause reaction between the two substances to give methane and atomic hydrogen.

Temperature Coefficient of Reaction of Free Radicals and Metals.—The effect of temperature on the rate of reaction of the free radicals with metallic mirrors is also interesting. In one experiment the times of removal of standard lead mirrors heated to various temperatures were measured. The results are shown in Fig. 13 as are also the results of a similar experiment using metallic antimony. The rate of combination of the free radicals with lead diminishes rapidly with rising temperatures; above 350° there is no action on the lead mirrors, though after allowing them to cool they can be readily removed.[9] This behavior is in striking contrast with that of the radicals on metallic antimony; in this case mirrors are readily removed even above 300°; in fact, the reaction seems to proceed quite readily up to temperatures beyond which further measurements are impossible due to the volatility of the antimony. This fact may possibly explain the failure of Paneth and Hofeditz to obtain free methyl radicals by substituting antimony trimethyl for lead tetramethyl in their original experiment.

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[8] These experiments afford further proof that atomic hydrogen is not present with the free radicals in the gases leaving the furnace.

[8a] See *Trans. Far. Soc.*, 30, 188 (1934).

[9] In one experiment it took 110 seconds to remove a lead mirror at 0° C.; however this long time of removal may be due to the formation of slight amounts of gummy substances which appear to form sometimes even at room temperature, and which make the results with lead mirrors somewhat erratic.

Products Formed by Interaction of Free Radicals and Metals.— The products formed by the combination of methyl and ethyl groups with the metals arsenic, antimony and bismuth have recently been studied in some detail. The free radicals were prepared[10] at low pressure in a stream of hydrogen by the thermal decomposition of tetramethyl or tetraethyl lead, and the hydrogen stream containing the free radicals was passed over the metallic mirror. The products were condensed in a liquid air trap and fractionally distilled, and the various metallic alkyls separated and identified. Experiments were carried out with the mirrors at different temperatures; the compounds obtained are shown in Table III.

TABLE III

COMPOUNDS FORMED BY REACTION OF FREE METHYL AND ETHYL WITH ARSENIC, ANTIMONY AND BISMUTH

Temperature of the Mirror.	Compounds formed	Arsenic.		Antimony.		Bismuth.	
		Methyl.	Ethyl	Methyl.	Ethyl	Methyl.	Ethyl
Cold	Tri-alkyls	$As(CH_3)_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	Di-alkyls	$[As(CH_3)_2]_2$	$[As(C_2H_3)_2]_2$	$[Sb(CH_3)_2]_2$			
	Mono-alkyls	$[As(CH_3)]_5$	$[As(C_2H_5)]_5$				
Hot	Tri-alkyls	$As(CH_3)]_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	Di-alkyls	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$[Sb(CH_3)_2]_2$	$[Sb(C_2H_5)_2]_2$	$[Bi(CH_3)_2]_2$	
	Mono-alkyls	$[As(CH_3)]_5$	$[As(C_2H_5)]_5$				

As a rule, heating the mirror increases the number of different products formed. This is to be expected if we remember that the less volatile di- and mono-alkyls can more readily leave the surface of the hot than of the cold mirrors. Dimethyl antimony can be obtained to a certain extent from the cold mirror but much more easily on heating, while its ethyl analog can be obtained only by reaction with a hot mirror. The dimethyl compound is the long looked for analog[11] of Bunsen's cacodyl. It is curious that this substance should have been prepared in the pure state for the first time by direct combination with free radicals in view of the previous unsuccessful attempts to prepare the pure compound by ordinary methods.

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[10] Paneth, *Proc. Far. Soc.*, **30**, 179 (1934).

[11] Morgan and Davies, *Proc. Roy. Soc.*, **A110**, 523 (1926).

The tendency to form organometallic compounds in which two metallic atoms are linked together seems to increase from left to right in the Periodic table. Whereas zinc, cadmium and mercury in Group II yield the simple compounds, R_2M, almost exclusively,[12] the subgroup elements of Group V, arsenic, antimony and bismuth yield organometallic compounds containing both single and linked metal atoms when methyl groups react with the hot mirrors, and tellurium, a metal of Group VI, yields only the double compound dimethyl ditelluride $CH_3TeTeCH_3$ and no dimethyl telluride $(CH_3)_2Te$ under similar conditions.[12a]

Decomposition and Interaction of Free Radicals.—When lead tetramethyl is decomposed at low pressures in a stream of hydrogen,[1] the products resulting from the recombination of the methyl radicals are not condensed by liquid air, which means that methane, ethane, ethylene, and hydrogen are the only possible products, since none of these would have been condensed under the experimental conditions. No further work was done with methyl groups, but the products resulting from the recombination of ethyl groups were carefully investigated.[2] Lead tetraethyl was decomposed in a stream of hydrogen; a liquid air trap was placed about 50-60 cm. from the furnace. The condensate was identified as *n*-butane from its vapor pressure curve and molecular weight, together with its lack of reactivity toward bromine; no other product that could be condensed by liquid air was formed in significant quantity. However, with the arrangement used, methane and probably also ethane and ethylene, would not be detected. From the amount of lead tetraethyl decomposed and the amounts of butane recovered it seems likely that the ethyl groups react also in some other manner, but the experiments do not permit us to estimate either the extent of the reactions or the products formed.

Other experiments on the decomposition of metal alkyls [13] yield further information on the products formed by the recombination of free radicals. It seems quite certain that the recombination of methyl groups to form ethane and of ethyl groups to form butane play a large part in such decompositions. There is also evidence that such reactions occur as

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[12] In the case of mercury there was some evidence of the formation of a very small quantity of an alkyl mercurous compound possibly $CH_3HgHgCH_3$. See Rice and Evering, *J. Am. Chem. Soc.*, 56, 2105 (1934).

[12a] Rice and Glasebrook, *J. Am. Chem. Soc.*, 56, 2472 (1934).

[13] Simons, McNamee and Hurd, *J. Phys. Chem.*, 36, 939 (1932); Whaley, *Ph. D. Thesis*, Johns Hopkins University, 1932; Meinert, *J. Am. Chem. Soc.*, 55, 979 (1933).

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 \text{ and}$$

$$C_2H_5 + C_2H_5 \rightarrow H_2 + 2\, C_2H_4.$$

The evidence for these, however, is not altogether conclusive because there also exists the possibility that the free radicals may react with the metallic alkyl and with the saturated and unsaturated hydrocarbons produced during the decomposition. It is probably not correct to assume that these products are stable in the presence of decomposing lead alkyls in the range 300-500° C.

It should be very interesting to investigate the decomposition products of lead or mercury alkyls carried in very minute quantities in an inert gas at about atmospheric pressure and heated in the range 550-750° C. If pyrogenic decompositions proceed through a chain mechanism, such an experiment must tell us the products formed when the chain is broken by collision of its carriers.

The decomposition of radicals has not been studied experimentally to any great extent, and it is therefore necessary to make various assumptions concerning their method of decomposition. It seems clear that methyl and ethyl groups have a higher stability than any other alkyl radicals, since all attempts to prepare these latter by the Paneth method have failed. It seems quite reasonable to assume that a propyl radical, for example, would readily decompose into ethylene and a free methyl group, and that all higher alkyl radicals could decompose similarly to yield olefines and either a methyl group, an ethyl group, or a hydrogen atom. In one experiment free methyl groups were carried in a current of ethylene in an attempt to reverse this process, but no propyl radicals were obtained,[14] though it seems very likely from other experiments[15] that larger alkyl radicals can exist at low temperature and under special conditions, but that under conditions of low pressure and somewhat high temperature they decompose rapidly. It may be possible to prove the presence of larger radicals by introducing atomic hydrogen into an excess of a hydrocarbon and examining the products formed by interaction with a metal. The success of such an experiment will depend upon finding a compound the energy of activation of whose reaction with atomic hydrogen is sufficiently smaller than the activation energy of the decomposition of the free radical formed.

From the fact that methyl radicals appear to be the only products of the decomposition of aldehydes, ketones, and ethers it seems likely that the larger radicals formed in the primary dissociation of these classes of compounds decompose readily. Furthermore, although the acetyl radical is presumably formed in the primary dissociation of acetone, no evidence of its recombination to diacetyl could be found when acetone was heated at low pressures.[14] It does seem plausible, however, that certain larger radicals, such as the isopropyl and tertiary butyl radicals, should have a somewhat higher stability (perhaps comparable with that of the ethyl group) than other large radicals, owing to the fact that they presumably have to decompose by the rupture of a C — H bond to produce atomic hydrogen and the corresponding olefin.

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[14] Rice and Evering, Unpublished work.

[15] Taylor and Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

In developing a mechanism for the decomposition of organic compounds it has been assumed that, in general, the larger radicals break down very readily, producing a smaller free radical plus compounds containing a double bond. It seems very much more probable that a radical will decompose in this manner than that it will dissociate into two smaller radicals. Fortunately, in the great majority of cases there is not more than one way in which a large free radical can decompose on this basis. In those few examples in which two methods of decomposition are possible[15a] it seems best at present to assume equal probability for both alternatives.

In brief, then, larger free radicals are supposed to break down finally into olefinic compounds and either methyl groups, ethyl groups, or hydrogen atoms; this process occurs normally through rupture of a C — C bond, which is, of course, entirely reasonable in view of the much higher strength of the C — H bond (see Chap. VI). Only in a few isolated cases has it been necessary to assume the rupture of a C — H bond.

Experimental evidence that the n-butyl and sec-butyl radicals decompose in this manner has recently been obtained. Frey and Hepp[16] decomposed di-n-butyl mercury and di-sec-butyl mercury by passing the vapors at about 3 mm. pressure through a pyrex tube heated to 490° C. The exit gases were analysed very completely by a distillation method[17] which had previously been used for studying hydrocarbon decompositions. No undecomposed mercury alkyl could be detected.

[15a] The secondary hexyl radical $CH_3CH_2CH_2CH(CH_2CH_3)—$ can decompose in two ways by rupture of a C—C bond to give either $CH_3CH_2CH_2CH{=}CH_2 + CH_3—$ or $CH_3CH_2CH{=}CH_2 + CH_3CH_2—$.

[16] Frey and Hepp, *J. Am. Chem. Soc.*, **55**, 3357 (1933).

[17] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

The experimental results of Frey and Hepp may be expressed by equations in which the products obtained per one hundred butyl radicals are calculated.

$$\begin{aligned} 100\,C_4H_9(n) = {} & 0.35\,CH_4 + 75.6\,C_2H_4 + 8.35\,C_2H_6 + 0.58\,C_3H_8 \\ & + 1.32\,C_4H_8(n) + 27\,C_4H_{10}(n) + 1.8\,[C_5H_{10} \\ & + C_5H_{12}] + 14.1\,C_6H_{14} + 2.8\,C_8H_{18}. \end{aligned}$$

$$\begin{aligned} 100\,C_4H_9(\text{sec.}) = {} & 1.7\,CH_4 + 0.63\,C_2H_6 + 10.7\,C_3H_6 + 0.62\,C_3H_8 \\ & + 16.2\,C_4H_8(n) + 15.8\,C_4H_{10}(n) + 0.32\,C_5H_{10} \\ & + 8.5\,C_5H_{12} + 1.08\,[C_6H_{12} + C_6H_{14}] \\ & + 0.59\,C_7H_{16} + 22.6\,C_8H_{18}. \end{aligned}$$

Omitting all products formed to the extent of less than 2% a calculation of the decomposition products of mercury di-n-butyl gives:

$$\begin{aligned} 100\,C_4H_9(n) = {} & 75.6\,C_2H_4 + 8.35\,C_2H_6 + 27\,C_4H_{10}(n) + 14.1\,C_6H_{14} \\ & + 2.8\,C_8H_{18}. \end{aligned}$$

It is clear that about three-quarters of the butyl radicals formed in the primary decomposition decompose according to the equation:

$$CH_3CH_2CH_2CH_2 \rightarrow C_2H_4 + CH_3CH_2;$$

the undecomposed butyl radicals partly combine with each other and partly with ethyl groups:

$$2\,CH_3CH_2CH_2CH_2 \rightarrow C_8H_{18}$$

$$CH_3CH_2CH_2CH_2 + CH_3CH_2 \rightarrow C_6H_{14}(n).$$

The remaining ethyl groups combine:

$$2\,CH_3CH_2 \rightarrow CH_3CH_2CH_2CH_3.$$

Judging from the relatively small quantities of ethane and of butene, the disproportionation reactions:

$$2\,CH_3CH_2 \rightarrow C_2H_4 + C_2H_6 \text{ and}$$

$$CH_3CH_2 + CH_3CH_2CH_2CH_2 \rightarrow CH_3CH_2CH{=}CH_2 + C_2H_6$$

do not occur to any marked extent. All of the important products found experimentally are therefore accounted for by the theory, and no absent products are predicted.

In the same way, again omitting all products formed to the extent of less than 2%, we obtain for di-sec-butyl mercury:

$$100\ C_4H_9(\text{sec}) = 1.7\ CH_4 + 10.7\ C_3H_6 + 16.2\ C_4H_8(\text{n}) + 15.8\ C_4H_{10}(\text{n}) + 8.5\ C_5H_{12}(\text{iso}) + 22.6\ C_8H_{18}.$$

Apparently the sec-butyl radical formed in the primary decomposition decomposes only to the extent of about 10% according to

$$CH_3CH_2CHCH_3 \rightarrow C_3H_6 + CH_3.$$

The undecomposed sec-butyl radicals partly combine with each other, partly disproportionate, and partly combine with methyl groups:

$$2\ CH_3CH_2CHCH_3 \rightarrow C_8H_{18}$$

$$2\ CH_3CH_2CHCH_3 \rightarrow C_4H_8(\text{n}) + C_4H_{10}(\text{n})$$

$$CH_3CH_2CHCH_3 + CH_3 \rightarrow CH_3CH_2CH(CH_3)_2.$$

The methyl groups undergo the disproportionation reaction

$$CH_3CH_2CHCH_3 + CH_3 \rightarrow CH_4 + C_4H_8$$

only to a slight extent; furthermore they do not combine to give ethane because of their small concentration relative to the sec-butyl radicals. Here again these equations account for all the principal products and do not predict any absent products.

It is of interest to compare the experimental results obtained with the lower lead alkyls when decomposed under these conditions.[13] When lead tetramethyl is decomposed at 550° C. and at 0.5-1.5 mm. pressure by a flow method, the combination of methyl groups to form ethane is the dominant reaction; in these experiments the rate of flow was sufficiently rapid that combination of the radicals took place outside the furnace. When lead tetraethyl is decomposed at 500° C. and 0.5 mm. pressure by a flow method and the results calculated as before per 100 ethyl groups produced in the primary dissociation we obtain:

$$100\ C_2H_5 = 28.6\ C_4H_{10} + 14.9\ C_2H_6 + 28.3\ C_2H_4 + 12.0\ H_2.$$

The main reaction is combination of the ethyl groups:

$$2\ C_2H_5 \rightarrow C_4H_{10},$$

accompanied by some disproportionation,

$$2\ CH_3CH_2 \rightarrow C_2H_4 + C_2H_6,$$

and a smaller amount of decomposition of the ethyl radical:

$$CH_3CH_2 \rightarrow C_2H_4 + H.$$

The hydrogen atom may then react either according to the equation

$$CH_3CH_2 + H \rightarrow H_2 + C_2H_4 \text{ or}$$
$$CH_3CH_2 + H \rightarrow C_2H_6.$$

It seems probable therefore that when a free radical is produced at about 500°, only a very few simple stoichiometric equations are necessary to describe the reactions that occur. The radical may either combine with itself or decompose into an unsaturated compound and a small free radical which in turn combines either with itself and with the larger radical; in addition both the radicals undergo disproportionation reactions to some extent.

Reactions of Free Radicals with Olefins.—It is clear from the previous discussion that reactions such as $CH_3CH_2CH_2 \rightarrow CH_3 + C_2H_4$ and $CH_3CH_2CH_2CH_2 \rightarrow CH_3CH_2 + C_2H_4$ must occur readily at higher temperatures; furthermore, recent work has shown [18] that these reactions are also reversible and that under conditions of lower temperature and higher pressure the back reaction occurs and larger free radicals are formed. This process repeats itself until two of the radicals collide and either combine or disproportionate to give stable molecules. Thus, in the work of Taylor and Jones,[18] varying proportions of free radicals (ethyl or methyl groups) were introduced into pure ethylene or into mixtures of ethylene and hydrogen. The total pressure was kept at approximately half an atmosphere and the temperature was in the range 250-300°, in which range ethylene neither polymerises nor reacts with hydrogen. The radicals were furnished by the decomposition of lead or mercury alkyls, which, at the temperatures used, break down into the metal and the free alkyl radicals. In one experiment (no. 14) in which pure ethylene was used, it was found that each ethyl radical added caused seven molecules of ethylene to disappear from the reaction. These were recovered in the form of an oil, produced presumably by some such reaction as:

$$7\,C_2H_4 + CH_3CH_2 \rightarrow CH_3CH_2(CH_2)_{14}$$
$$2\,CH_3(CH_2)_{15} \rightarrow CH_3(CH_2)_{30}CH_3.$$

The first of these reactions consists of successive additions of ethylene molecules to an ethyl radical followed by combination or disproportionation of the large radicals formed in this way. Possibly also these reactions are accompanied to a greater or less extent by decomposition of the larger free radicals into smaller radicals and cycloparaffins (see p. 85) since there is now a considerable amount of experimental evidence that naphthenic hydrocarbons are among the products formed when ethylene is polymerised [18a] under various conditions.

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[18] Taylor and Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930); Cramer, *ibid.*, **56**, 1234 (1934). See also in this connection the work of Taylor and Hill, *J. Am. Chem. Soc.*, **51**, 2922 (1929) on hydrocarbon reactions with excited mercury.

Cramer [19] has studied the reactions of free ethyl groups with ethylene in the liquid phase at high pressures (14-80 atmospheres) in the temperature range 180-240°. Lead tetraethyl was used as the source of ethyl groups and the decomposition was carried out in benzene solution; the benzene did not enter into the reaction and could be recovered unchanged. In the first six experiments, approximately 0.4 moles of ethyl groups were introduced either into pure benzene or into benzene in the presence of hydrogen. Somewhat less than half of these groups appeared as ethane, the remainder forming an oil; there were also small quantities of gaseous olefins, and a small quantity of hydrogen and butane. The experiments performed in the presence of hydrogen showed that this gas had no appreciable effect on the nature of the products.

These results indicate that the predominating reaction in the decomposition of pure tetraethyl lead under these conditions is the disproportionation reaction,

$$2\,CH_3CH_2 \rightarrow C_2H_4 + C_2H_6,$$

followed by polymerisation of the ethylene by the ethyl groups, presumably according to some such scheme as that suggested by Taylor and Jones.

When an excess of ethylene was present at the commencement of the decomposition, the formation of ethylene polymers was, as might be expected, greatly increased. In one of Cramer's experiments (no. 14) 0.002 moles of ethyl groups were introduced in the presence of 0.6 moles of ethylene. No ethane, butane or hydrogen was formed and 90% of the ethylene appeared as an oil. A calculation showed that each ethyl group introduced had caused the polymerisation of 225 ethylene molecules.

[18a] Collie, *J. Chem. Soc.*, **87**, 1540 (1905); Ipatiew, *Ber.*, **44**, 2978 (1911); Dunstan, Hague and Wheeler, *J. Soc. Chem. Ind.*, **51**, 131T (1932); Storch, *J. Am. Chem. Soc.*, **56**, 374 (1934).

[19] Cramer, *J. Am. Chem. Soc.*, **56**, 1234 (1934).

Reactions of Free Radicals with Organic Molecules.—Assuming that the thermal decomposition of such substances as acetaldehyde, acetone, and butane occurs to some extent at least through a free radical mechanism, we must conclude from a study of the chemical products formed, that there is one type of reaction between free radicals and molecules which does not occur to an appreciable extent under the conditions of temperature and pressure ordinarily used, namely temperatures above 500° and atmospheric or lower pressure. This type of reaction may be illustrated by the following equations:

$$CH_3 + CH_3CHO \rightarrow CH_3CH_3 + CHO$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_3CH_3 + CH_3CO$$

$$CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CH_2;$$

it consists of the rupture of a C — C linkage by reaction with the free radical and results in the production of a saturated molecule.. The conclusion that such reactions do not occur very readily is based on the fact that ethane is not formed in appreciable quantities during the thermal decomposition of acetaldehyde or acetone, nor is propane formed to an appreciable extent [20] in the thermal decomposition of butane induced by methyl radicals. The evidence against this type of reaction is strengthened by Leermakers' discovery [21] that the products of the photochemical decomposition of acetaldehyde at higher temperatures, which is almost certainly a chain reaction, are identical with the products of the ordinary thermal decomposition, consisting in both cases entirely of methane and carbon monoxide. It seems best therefore to omit consideration of this type of reaction for all classes of organic compounds of low molecular weight, when they are decomposed at pressures of atmospheric or lower and at temperatures not greatly below 450-500°.

From the point of view of steric considerations, the reaction

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$$

would be preferred to the reaction

$$CH_3 + CH_3CHO \rightarrow CH_3CH_3 + CHO.$$

If the effect of the steric factor were equivalent to an increase in activation energy of only eight or ten calories, this would be sufficient (if otherwise the reactions went with the same activation energy) to make the second reaction negligibly slow in comparison with the first. This matter will be discussed in greater detail in the following chapter.

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[20] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

[21] Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

Other reactions of this type that we omit from consideration are the corresponding reactions with ethers:

$$CH_3 + CH_3OCH_3 \rightarrow CH_3CH_3 + CH_3O$$

$$CH_3 + CH_3CH_2OCH_2CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CH_2O.$$

In general, then, the interpretation of the decomposition of organic compounds from a free radical standpoint demands that we exclude consideration of the attack of the free radicals on the C — C chain; this leaves then, as the only reaction to be considered, the removal of hydrogen atoms from the substrate molecule by the free radicals. This reaction is followed by decomposition of the radical formed from the substrate molecule and the formation of a smaller free radical which is regenerated in each chain cycle. Since there are usually different kinds of hydrogen atoms (primary, secondary, tertiary) present in a molecule, there will also be several chain cycles occurring simultaneously and generating different products; the number of chain cycles and the number of different products are therefore determined by the number of different kinds of hydrogen atoms in the substrate molecules. The detailed discussion of these mechanisms will be presented in the following chapters.

Bivalent Radicals.—The properties of the methylene radical have already been discussed (p. 52) in connection with its preparation and it is only necessary to add here that its half life, as judged by the time taken to remove standard mirrors placed at different distances from the furnace, is of the same order as that of the alkyl radicals, namely a few thousandths of a second.

The radical $\underset{|}{CH_2} - \underset{|}{CH_2}$ has been mentioned[22] from time to time in the literature but an attempt to demonstrate its existence by heating ethylene at low pressure to about 1000° C. and then bringing the gas rapidly in contact with a cold antimony mirror failed;[23] if this radical is formed at all either it does not attack an antimony mirror or it has an exceedingly short life.

Similar remarks probably apply to the ethylidene radical, CH_3CH, since an attempt[24] to prepare it from diazoethane gave a negative result. Furthermore, this radical apparently isomerises with great ease, producing a molecule of ethylene. It is curious that the reaction

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[22] See Hurd, *Ind. Eng. Chem.*, 26, 50 (1934).

[23] Rice and Whaley, *J. Am. Chem. Soc.*, 56, 1311 (1934).

$$CH_3CH \rightarrow CH_2{=}CH_2$$

occurs with a much lower activation energy than the reaction

$$CH_3CH \rightarrow H_2 + CH{\equiv}CH$$

which is also exothermic to the extent of about 20 Cal., but this must be assumed from the fact that only ethylene, and no acetylene, is found among the decomposition products of diazoethane. It seems not unlikely that all bivalent radicals of the general formula $RR_1C <$ will be found to rearrange either spontaneously or with a very low activation energy to the corresponding olefine.[25] The radical $\underset{|}{C}H_2CH_2\underset{|}{C}H_2$ probably isomerises very easily to form propylene:

$$\underset{|}{C}H_2CH_2\underset{|}{C}H_2 \rightarrow CH_3CH{=}CH_2$$

and similarly the radical $\underset{|}{C}H_2CH_2CH_2\underset{|}{C}H_2$ probably gives 2-butene although it might also decompose into ethylene. Both of these reactions,

$$\underset{|}{C}H_2CH_2CH_2\underset{|}{C}H_2 \rightarrow CH_3CH{=}CHCH_3$$

$$\underset{|}{C}H_2CH_2CH_2\underset{|}{C}H_2 \rightarrow 2\,C_2H_4$$

are probably strongly exothermic.

It may be found to be a general rule that a radical, which is isomeric with a molecule, requires little or no activation energy to isomerise if the process can take place by migration of an atom or group to an adjoining atom.

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[24] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 741 (1934).

[25] It will be interesting to test whether a methyl group will migrate in the bivalent radical $(CH_3)_3CH <$ to give trimethyl ethylene. This work is now in progress in collaboration with Professor F. C. Whitmore.

CHAPTER VI

ACTIVATION ENERGIES OF ELEMENTARY REACTIONS

The first essential in a study of the pyrogenic decomposition of organic compounds is a knowledge of the strength of bonds, for it is of course logical to assume that a molecule will break first at its weakest bond. We must remember however that we are interested primarily in (1) the activation energy[1] of the process which consists of the rupture of a bond and the consequent dissociation into two fragments, (2) the activation energies of the various possible reactions between the fragments thus produced and undecomposed molecules, (3) the activation energies of the reactions between the fragments themselves and (4) the activation energies of the decompositions of the fragments.

Thermochemical Estimates.—The earlier attempts, by Fajans and others, to measure the strengths of bonds[1a] were based essentially on thermochemical estimates of the heats of combination of gaseous atoms. If we write the necessary equations using the more modern values for the different quantities we obtain:

$$\begin{array}{rclr}
 & & & \Delta H \\
C(\text{graphite}) + 2H_2(g) & \rightarrow & CH_4(g) & -\ 18.5\ \text{Cal.[2]} \\
4H(g) & \rightarrow & 2H_2(g) & -205\ \ \text{Cal.[3]} \\
C(\text{gas}) & \rightarrow & C(\text{graphite}) & -154\ \ \text{Cal.[4]} \\
\hline
C(\text{gas}) + 4H(g) & \rightarrow & CH_4(g) & -377.5\ \text{Cal.}
\end{array}$$

This gives a value of 94.4 Cal. for each $C-H$ bond in methane. A similar calculation for ethane gives,

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[1] There are several definitions of activation energy (see Kassel, *Homogeneous Gas Reactions,* Chemical Catalog Co., 1932) but our estimates are too rough to warrant consideration of these differences. The activation energy of a dissociation process cannot be smaller than the bond strength and probably in general has a slightly higher value.

[1a] Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922); see also Weinberg, *ibid.*, **53**, 1347, 1353, 1519 (1920); W. Hückel, *ibid.*, **55**, 2839 (1922); Thiel, *ibid.*, **55**, 2844 (1922).

[2] Mayer and Altmayer, *Ber.*, **40**, 2134 (1907).

[3] Weizel, *Bandenspektren*, p. 249. Leipzig, 1931.

[4] Kistiakowsky and Gershinowitz, *J. Chem. Physics*, **1**, 432 (1933).

	H
$2C(\text{graphite}) + 3H_2(g) \rightarrow C_2H_6(g)$	— 23.4 Cal.[5]
$6H(g) \rightarrow 3H_2(g)$	— 307.5 Cal.
$2C(\text{gas}) \rightarrow 2C(\text{graphite})$	— 308 Cal.
$2C(g) + 6H(g) \rightarrow C_2H_6(g)$	— 638.9 Cal.

Assuming that the strengths of the C — H bonds in ethane are approximately the same as those in methane we obtain 638.9 — (6 × 94.4) = 72.5 Cal., for the strength of the C — C bond in ethane. Underlying all such calculations is the assumption that the binding energies of the different bonds in methane and the other hydrocarbons are approximately independent of one another. This assumption appears very plausible when we consider the additivity of the heats of formation of methane and of the four hydrocarbons [6] formed by successive substitution of a methyl group for each of the hydrogen atoms of methane. The heats of combustion for these five hydrocarbons are:

CH_4	Methane	210.8
CH_3CH_3	Ethane	368.4
$CH_2(CH_3)_2$	Propane	526.3
$CH(CH_3)_3$	Isobutane	683.4
$C(CH_3)_4$	Neopentane	842.6

The differences for the four successive substitutions are 157.6, 157.9, 157.1, 159.2 respectively.

This assumption of the equality of the four bonds in methane has been questioned by Mecke.[7] He states: " We will have to picture the decomposition of methane and of other saturated hydrocarbons, in such a way that the removal of the first hydrogen involves the greatest energy (more than 100 Cal.) ; that of the second would be less, because here the formation of divalent from tetravalent carbon must be taken into account, and methylene (CH_2) will have a certain stability, similar to that of CO."

Recently Rossini [7a] has measured the heats of combustion of a number of normal paraffin hydrocarbons very accurately and has discussed their bond energies in the light of these new data. He found that for normal hydrocarbons containing more than five carbon atoms there is a linear relationship between the heats of combustion and the number of carbon atoms, but for lower hydrocarbons there is appreciable deviation from linearity. He concludes from his measurements that the dissociation energy of a normal gaseous hydrocarbon C_nH_{2n+2} into gaseous carbon and hydrogen atoms is not a linear function of n below $n = 6$ but is a linear function of n above this value. The explanation adopted for this deviation is that the strength of a given C — H or C — C bond is dependent in the first place on the adjacent bonds and in the second place (but to a much less extent) on the bonds once removed from the bond in question. On this basis C — H or C — C bonds in the interior of a long chain are equivalent but differences exist for those bonds attached to the end- and next to the end-carbon atoms and to a much less extent for C — H bonds in the 3 position. However the data indicate that these differences are relatively small and amount at most to a maximum change in the strength of a bond of only a few per cent.

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[5] International Critical Tables.

[6] See Kharasch, *B. S. Jour. of Research*, **2**, 359 (1929).

[7] Mecke, *Z. physik. Chem.*, [B]7, 108 (1930) ; see also Iredale and Mills, *Nature*, **126**, 604 (1930).

[7a] Rossini, *Proc. Nat. Acad. Sci.*, **20**, 323 (1934) ; *idem, Bur. Stand. J. Res.*, **13**, 21 (1934).

Recent measurements of bond strengths by quite independent methods have yielded values which are in close agreement with those first estimated from thermochemical data. Conant[8] has used measurements of Ziegler[9] to estimate the strength of the ethane C — C bond in various substituted ethanes. On the assumption that the effects of substitution are approximately additive he calculated the heat of dissociation of the carbon atoms in ethane to be 76.5 Cal. The thermal dissociation of cyanogen into two cyanide radicals has also been measured[10] recently; the method consists essentially in measuring the concentration of cyanide radicals at different temperatures by means of their absorption spectrum and then calculating the heat of the reaction by the van't Hoff isochore. The value obtained was 77 ± 4 Cal. If we assume that in simple aliphatic compounds the strengths of C — H and C — C bonds are approximately independent of the compound in which they occur, this value also agrees very well with the early estimates. Furthermore, the strength of the C — H bond in hydrocyanic acid, as calculated from the value for the dissociation of cyanogen and other thermochemical data, was found to be 94.5 Cal., which is also in good agreement with the early thermochemical calculations.

Pauling[11] has recently calculated the strengths of a number of bonds in organic molecules from experimental values of the heats of formation and combustion of the gaseous molecules; the following are some of the values obtained:

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[8] Conant, *J. Chem. Physics*, 1, 427 (1933).

[9] Ziegler, *Ann.*, 473, 163 (1929).

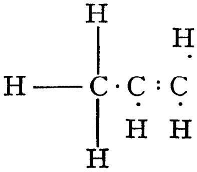
[10] Kistiakowsky and Gershinowitz, *J. Chem. Physics*, 1, 432 (1933).

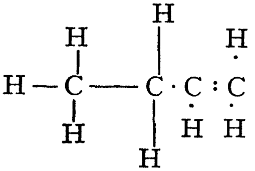
[11] Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

C — H (Hydrocarbons)	100 Cal.	C — O (Alcohols, ethers)	82 Cal.
C — C (Hydrocarbons)	82.5 Cal.	C — N (Amines)	66 Cal.
C = C (Hydrocarbons)	145 Cal.	C ≡ N (Nitriles, HCN	203 Cal.
C ≡ C (Hydrocarbons)	200 Cal.	C — Cl (Alkyl halides)	78 Cal.

Effect of Substitution and Structure on Bond Strength.—The most casual survey of chemical reactions shows that the substitution of atoms or groups in molecules for other atoms or groups may enhance or diminish chemical reactivity, often to a striking degree, and we may reasonably infer from this behavior that the strength of a particular bond is affected by the atoms or groups contiguous to it in the molecule. Substitution of three of the hydrogen atoms of methane by methyl groups produces isobutane $(CH_3)_3CH$, the tertiary hydrogen atom of which is undoubtedly much more reactive, and therefore presumably less strongly bound than the hydrogen atoms in methane. This same effect is shown in still greater degree by the two compounds methyl alcohol and tertiary butyl alcohol.

There is probably only a small difference in strength between the primary, secondary, and tertiary C — H bonds in saturated hydrocarbons;[12] however, with unsaturated compounds the effect of the double or triple bond on the adjoining C — C and C — H bonds in the molecule is such that the differences are much more pronounced. It seems to be a general rule that when there is a doubly bound carbon atom in a molecule, the bonds in the alpha position to this bond are much stronger than normal, whereas those in the beta position are much weaker; this may be represented for propylene and 1-butene by the following formulas in which strong bonds are represented by points and weak bonds by longer lines:





—— weak bonds; — normal bonds; · strong bonds.

This same effect is also shown in the aliphatic ketones and aldehydes in which the alpha hydrogen atoms[13] are more than usually reactive; according to the above notation, acetone, methyl ethyl ketone and acetaldehyde would be represented as follows:

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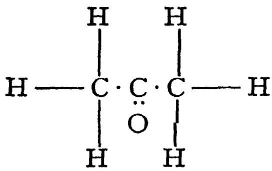
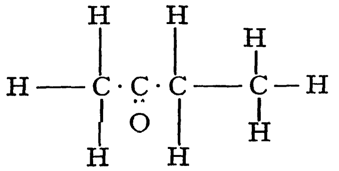
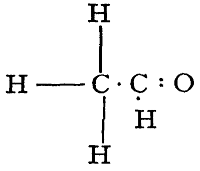
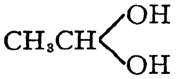
[12] See Brackett, *Proc. Nat. Acad. Sci.*, **14**, 857 (1928).







However, evidence based on chemical reactivity must be applied with caution, as may be realized by considering the hydrogen atom of the aldehyde group in acetaldehyde; according to these rules it should be more strongly bound than a hydrogen atom in a hydrocarbon, yet in solution oxidation occurs readily and this hydrogen is replaced by the OH group. This process will be discussed in detail later (p. 179); however we may point out that it is probably a chain reaction, possibly proceeding through the intermediate formation of  $CH_3CH\begin{matrix}OH\\OH\end{matrix}$, so that in all probability we are not justified in assuming, because it is easily oxidized, that the aldehyde C — H bond is weak. This placing of strong and weak bonds in a molecule seems to be a general rule[14] and is useful in making estimates of the activation energies of processes involving either rupture of the molecule or its reaction with free radicals. The influence of an unsaturated grouping extends only to the bonds in its immediate neighborhood; it is only the α-hydrogen atoms in aldehydes, ketones, acids, and esters that show unusual chemical reactivity towards halogens and in condensations of the Claison type that these substances undergo. Examination of the ultraviolet absorption spectra of the aliphatic ketones[15] indicates that the effect of the carbonyl groups extends only to adjacent bonds. That is, the center of absorption of a pure liquid ketone is affected only by the substitution of an α or a β hydrogen atom; for example, substitution of an α-hydrogen atom in acetone to give methyl ethyl ketone causes the center of absorption to shift 23 Å.U. toward the red. The substitution of a β-hydrogen atom in methyl ethyl ketone to give methyl propyl ketone causes a further shift of 20 Å.U., but substitution of a γ-hydrogen atom is without effect. All ketones having the general formula $CH_3COCH_2CH_2R$, where R is an alkyl radical, have absorption bands with the center at the same position. In all the ketones investigated, substitution of hydrogen atoms beyond the β position was found to have no effect on the absorption band.

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[13] These C — H bonds are actually in the beta position to the carbonyl double bond.

[14] See however in this connection Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

[15] Rice, *Proc. Roy. Soc.*, **A91**, 76 (1914).

Arnold and Kistiakowsky [16] have recently shown that two such groups as the carbonyl and phenyl groups have a mutual influence over each other's spectra which extends only through carbon chains not more than two atoms long. At greater distances in the molecule the spectra become entirely independent of each other.

Activation Energies from Kinetic Measurements.—According to the free radical theory the thermal decomposition of aliphatic compounds may be explained on the basis of a chain mechanism; therefore the measured activation energy of the overall reaction is not only that of the primary decomposition into free radicals but is a composite quantity into which the activation energies of the various intermediate reactions also enter. It is of course possible to make estimates of the activation energies of the different steps [17] that are in agreement with the measurements for the overall reaction, but until such estimates have been checked by direct measurements of the elementary reactions involved, they must be regarded as very uncertain. There are a few reactions, such as the decomposition of azomethane and other aliphatic azo compounds (p. 140), of cyclopropane and some other cyclic compounds (p. 160), of the lower members of the olefin series (p. 123), and of the aliphatic nitrites (p. 138), that probably do not involve a chain mechanism, and therefore in these special cases the measured activation is approximately the same as that of the primary dissociation into two radicals.

Sometimes we can obtain information regarding the stability [17a] of a radical by considering the activation energy of the thermal decomposition which produces it; for example, methyl groups must be more stable than most aliphatic molecules since they are produced even in the decomposition of methane.[18] On the other hand, ethyl radicals are more stable than tetraethyl lead because they can be produced from it,[19] but they are not so stable as butane or diethyl ether because the decomposition of these compounds produces mainly methyl groups.[20] The introduction of free radicals produced either thermally[21] or photochemically[22] into an organic compound, followed by a measurement of the amount of induced reaction, also permits estimates of the activation energies of the elementary reactions involved.

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[16] Arnold and Kistiakowsky, *J. Am. Chem. Soc.*, **54**, 1713 (1932).

[17] See Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

[17a] In this paragraph we refer to the stability of radicals with reference to the products formed by their thermal decomposition.

[18] Rice and Dooley, *J. Am. Chem. Soc.*, **56**, 2747 (1934).

[19] Paneth and Lautsch, *Ber.*, **64**, 2702 (1931).

All the foregoing methods have the serious drawback that they do not measure the activation energies of the individual reactions directly but depend in each case on a knowledge of the mechanism, which is frequently very uncertain. It is possible, however, to measure the activation energy of the dissociation process into free radicals directly by the Paneth effect on metallic mirrors.[23] An organic compound is passed through a furnace at low pressures and the time of removal of a standard mirror at the end of the furnace is determined; for low percentage decompositions, the time of removal of the mirror is a measure of the concentration of the free radicals and hence of the velocity constant of the dissociation process. When this experiment is repeated with the furnace at another measured temperature it is possible to calculate the activation energy of the process from the Arrhenius equation. In the actual experiment the standard mirrors are placed at measured distances from the end of the furnace and the time of disappearance for zero distance is obtained by extrapolation.[24] The values obtained for a number of different compounds are shown in Table IV.

TABLE IV

ACTIVATION ENERGY OF THE DISSOCIATION INTO FREE RADICALS

Compound	E	Compound	E (Cal.)
Methane	100	Propane	71.5
Ethane	79.5	*n*-Butane *	65.4
Dimethyl Ether	81.1	*n*-Heptane *	63.2
Trimethyl amine	50.8	Acetone	70.9
Ethylene oxide	44.0	Ethyl alcohol **	68.6
Dimethyl Carbonate	74.4	Diethyl ether *	68.6

* Values for these larger molecules are probably somewhat low due to olefin formation; the olefins have a C — C bond somewhat weaker than that in the paraffin hydrocarbons.

** Possibly the low value for ethyl alcohol may be due to heterogeneous decomposition.

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[20] Rice and Glasebrook, *J. Am. Chem. Soc.*, 56, 2472 (1934).

[21] Frey, *Ind. Eng. Chem.*, 26, 198 (1934); Sickman and Allen, *J. Am. Chem. Soc.*, 56, 1251 (1934).

[22] Leermakers, *J. Am. Chem. Soc.*, 56, 1537 (1934); *idem, ibid.*, 56, 1899 (1934).

[23] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929); Rice and Johnston, *J. Am. Chem. Soc.*, 56, 214 (1934).

[24] This is necessary in order to avoid volatilization of the mirror by the heat of the furnace.

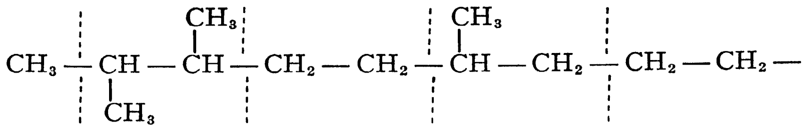
From the values for the first four compounds we obtain the activation energies associated with the four different kinds of bonds:

C — H bond:	$CH_4 \rightarrow CH_3 + H$	100.0 Cal.
C — C bond:	$C_2H_6 \rightarrow 2\,CH_3$	79.5 Cal.
C — O bond:	$CH_3OCH_3 \rightarrow CH_3O + CH_3$	81.1 Cal.
C — N bond:	$(CH_3)_3N \rightarrow (CH_3)_2N + CH_3$	50.8 Cal.

The further development of this method will permit not only the direct measurement of the activation energy of the primary decomposition but also of reactions between free radicals and molecules. Thus, if the methylene radical is carried in a current of ether it is found that above a certain temperature it reacts with the ether to form the methyl radical; the activation energy of the reaction was estimated[25] to be approximately 15 Cal.

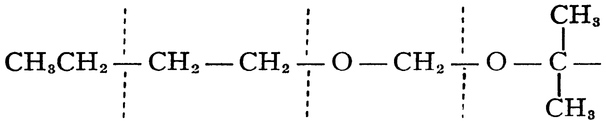
The experiments of Polanyi and his co-workers on elementary reactions between metallic sodium and alkyl halides have already been mentioned (p. 31); these experiments also permit a direct measurement of the activation energies of the elementary ractions involved.

Decomposition of Radicals.—Large aliphatic radicals may be regarded as consisting of a methyl or an ethyl group built up into a larger unit by being coupled with molecules containing a double bond; the double bond opens and in this way a radical of any degree of complexity may be built up by a coupling process. The following are examples in which the dotted lines show the boundaries of the constituent molecules:



$$CH_3 \,\vdots\, \underset{CH_3}{\underset{|}{CH}} - \overset{CH_3}{\overset{|}{CH}} \,\vdots\, CH_2 - CH_2 \,\vdots\, \overset{CH_3}{\overset{|}{CH}} - CH_2 \,\vdots\, CH_2 - CH_2 -$$

methyl, 2-butene, ethylene, propylene, ethylene



$$CH_3CH_2 \,\vdots\, CH_2 - CH_2 \,\vdots\, O - CH_2 \,\vdots\, O - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} -$$

ethyl, ethylene, formaldehyde, acetone

It is not surprising that the activation energies of the decompositions of such radicals are low, because it is to be expected that the constituent molecules would split off very readily. No measurements are available for any of these decompositions, but the failure to prepare hydrocarbon fragments larger than ethyl from the corresponding lead alkyls indicates that these higher radicals have a low energy of decomposition, probably less than 30 Cal. per mole. The estimates that have been made for these decompositions were selected [26] on the basis that they agreed best with the free radical mchanism.[27]

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[25] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).

Interaction of Radicals and Organic Molecules.—No direct measurements have yet been made of the activation energy of a process of this kind. The simple reaction

$$H + H_2 \text{ (para)} \rightarrow H_2 \text{ (ortho)} + H$$

has, however, been thoroughly studied [28] and has been found to have an activation energy of 7.2 Cal. On the other hand, the activation energy of the parallel reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

is not yet certain, although it is probably higher than the value of 8 Cal. reported by Hartel and Polanyi.[29] Leermakers has decomposed lead tetraethyl in the presence of hydrogen and has concluded that the reaction

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

has an activation energy [30] greater than 15 Cal.

There is no direct experimental evidence at all as to the values of the activation energies of the reactions of methyl and ethyl groups with organic molecules. Since chains are initiated when radicals are introduced into such substances as butane or acetaldehye at temperatures below their decomposition points, the activation energies must be low; estimates can be made by drawing up mechanisms which agree with the overall measurements.[31] In order to make the results of such mechanisms agree with the chemical products of the reactions it is necessary to postulate that reactions between the methyl or ethyl radicals and the carbon atoms of the substrate molecule have a relatively high activation energy as compared with that of reactions between the radicals and the hydrogen atoms of the substrate. For example, if E_1, E_2 and E_3 represent the activation energies of three possible reactions between a normal butane molecule and a methyl group,

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[26] Rice, *J. Am. Chem. Soc.*, 56, 488 (1934).

[27] It is curious that while the acetyl group is probably very unstable ($E = 10$ Cal. for the reaction $CH_3CO \rightarrow CO + CH_3$) the acetonyl radical appears to be more stable than many compounds ($E = 48$ for the reaction $CH_3COCH_2 \rightarrow CH_2 = CO + CH_3$) and would have a very long life if it did not react with itself or with other radicals present in the reaction mixture. See p. 113.

[28] Geib and Harteck, *Z. physik. Chem.*, Bodenstein-Festband, 849 (1931).

[29] Hartel and Polanyi, *Z. physik. Chem.*, 11B, 97 (1930); see also *Trans. Far. Soc.*, 30, 187, 246 (1934).

[30] Leermakers, *J. Am. Chem. Soc.*, 55, 4508 (1933).

[31] Rice and Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934); Leermakers, *ibid.*, 56, 1537, 1899 (1934).

$$CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_4 + CH_3CH_2CH_2CH_2— \qquad E_1$$

$$CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_4 + CH_3CH(CH_2CH_3)— \qquad E_2$$

$$CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_3 + CH_3CH_2CH_2— \qquad E_3$$

E_3 must be at least 10 Cal. greater than either E_1 or E_2 in order to account for the absence (save possibly small traces) of propane among the products of the interaction of methyl groups from mercury dimethyl with butane.[21] The value of 10 Cal. is a minimum for the value $E_3 — E_1$ or $E_3 — E_2$, actually the difference may be much greater than this (see p. 85). Other examples of reactions in which a radical might break the carbon skeleton of a molecule are:

$$CH_3 + CH_3CHO \rightarrow CH_3CH_3 + CHO$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_3CH_3 + CH_3CO$$

$$CH_3 + CH_3CH_2OCH_2CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CH_2O$$

$$CH_3CH_2 + CH_3N{=}NCH_3 \rightarrow CH_3CH_2CH_3 + CH_3N{=}N—.$$[32]

Such reactions have been excluded by assigning in each case a sufficiently high steric factor which probably plays a large part in decreasing the rates of these reactions. This steric factor[32a] is equivalent to an increase in activation energy of approximately 10 Cal. for the reaction $Na + (CN)_2 \rightarrow NaCN + CN$; measurements of the temperature coefficient (which is almost negligibly small) indicate that the activation energy is not more than 2 Cal., but from measurements of the actual rate of the reaction the activation energy appears to be about 12 Cal. Presumably the nitrogen atoms exert a shielding action and lower the rate of rupture of the C — C bond by the sodium atoms.

In the interaction of radicals and organic molecules we postulate therefore that all reactions involving the rupture of the carbon skeleton of the substrate by the free radicals have a sufficiently high activation energy that they can be neglected in comparison with the reactions between the free radicals and the hydrogen atoms attached to the carbon skeleton.[33] Although there are no direct measurements of these activation energies we can arrive at estimates which are probably reasonably accurate from the following considerations: (1) The activation energies assigned must lead to agreement with the actual chemical products. Analysis of the products of a reaction which proceeds through a chain mechanism enables the assignment of relative activation energies with considerable accuracy and the great variety of decompositions which are similar in mechanism makes this method of estimation very important and useful. (2) The strengths of the different C — H bonds are determined partly by the structure of the carbon skeleton and partly by substituents other than hydrogen atoms attached to it. Estimates of the strengths of these bonds can be made in the various ways discussed earlier in this chapter; it is probably correct to assume a parallelism between the strengths of the different C — H bonds and the activation energies of the reactions with free radicals. Reaction between a free radical and a more strongly bound hydrogen atom (e. g. one in the α position to a double bond) should require a higher activation energy than is required for reaction with a more weakly bound hydrogen atom, such as one in the β position to a double bond. Estimates based on these considerations must agree with those based on the nature of the chemical products as well as with the statement immediately following. (3) The activation energies assigned must lead to values for the rate and temperature coefficient of the overall reaction as well as of the reverse reaction which are in agreement with experimental measurements.

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[32] Leermakers (*J. Am. Chem. Soc.*, 55, 4508 (1933)) has shown that ethyl groups do not react with azomethane at 275° after 10^7 collisions.

[32a] Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930).

We have based estimates of the activation energies of different radical-molecule metatheses on the foregoing considerations and have applied them in the following chapters, which contain a detailed discussion of reaction mechanisms for different classes of compounds.

Interaction of Radicals with each other.—We may illustrate this type of reaction with reference to the ethyl radical as follows:

$$CH_3CH_2 + CH_3CH_2 \rightarrow CH_3CH_2CH_2CH_3 \qquad E_1$$

$$CH_3CH_2 + CH_3CH_2 \rightarrow C_2H_6 + C_2H_4 \qquad E_2$$

$$CH_3CH_2 + CH_3CH_2 \rightarrow H_2 + 2\,C_2H_4. \qquad E_3$$

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[33] See p. 69 for a fuller discussion of this problem.

All these reactions are strongly exothermic (40-80 Cal.) so that we might expect them to occur with little or no energy of activation. A qualitative experiment showed[33a] that methyl radicals must combine very easily because they do not diffuse through butane at 10-20 mm. pressure from the hot surface at which they are produced to an antimony mirror placed a few mm. away. The chemical evidence available indicates quite clearly that both combination and disproportionation can occur; however, the evidence for the third reaction is not so easily established because decomposition of the ethyl radical would yield the same products.

In a recent paper[34] an activation energy of 8 Cal. has been assigned to all reactions of these three types in order to make the proposed reaction mechanism agree with the experimental measuremnts; in addition a steric factor of about 10^{-1} in the velocity constants of these reactions has been assumed.

Activation Energies of Migration Processes.—There is an immense literature on molecular rearrangements[35] and yet we do not know at present to what extent they occur directly, or through a free radical mechanism, or through some such mechanism as suggested by Meer and Polanyi.[36]

The fact that the reaction

$$CH_3CHO \rightarrow CH_4 + CO$$

is exothermic to the extent of 22 Cal. might suggest that the migration of the aldehyde hydrogen atom to form CH_4 and CO should occur with little or no activation energy, whereas actually it requires at least 45.5 Cal.[37] and possibly much more than this, if the ordinary thermal decomposition is entirely a radical chain reaction. Similarly the thermal decomposition of acetone to produce methane and ketene,

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO$$

is exothermic to the extent of about 12 Cal., but the migration of a hydrogen atom from one carbon atom to another requires[38] a minimum of approximately 70 Cal. If an inhibitor for the thermal chain decompositions of organic compounds can be found it will be possible to determine whether the migration process goes simultaneously with the chain reaction [39] or whether it has a higher activation energy. The contrast between the ease with which a hydrogen atom in the ethylidene radical [40] seems to migrate to the adjoining carbon atom and the difficulty with which a similar process occurs in organic molecules is striking and suggests that the free valencies in the ethylidene radical may explain this difference in behaviour.

[33a] Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3529 (1932).

[34] Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

[35] *Molecular Rearrangements*, by Porter, Chemical Catalog Co., 1928.

[36] Meer and Polanyi, *Zeit. physik. Chem.*, **B19**, 164 (1932).

[37] This value is the measured activation energy of the overall decomposition. Fletcher and Hinshelwood, *Proc. Roy. Soc.*, **A141**, 41 (1933).

[38] The measured value of Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, **A111**, 245 (1926) for this decomposition.

Calculation of Rates of Elementary Reactions: — The rate of combination k' of c_1 and c_2 in the equilibrium,

$$c_1 + c_2 \rightleftarrows c_3$$

is given [41] approximately by the expression: $k' = Ae^{-E'/RT}$ where A is the total number of collisions one molecule makes per second and E' is the activation energy of the combination process. The constant A is equal to the average speed divided by the mean free path and very approximately has the value 10^9 for 1 mole in 24 liters (1 atmosphere at 27° C.) which is the unit used in these calculations. An exception to this expression occurs in the case of the recombination of gaseous atoms which require triple collisions; at atmospheric pressure this necessitates a factor of 10^{-3} which gives $10^6\, e^{-E'/RT}$ for the rate of combination under these conditions.

On the other hand, the rate of dissociation of c_3 in the above equilibrium is given by the expression

$$k = Be^{-E/RT}$$

where B seems to be of the order of magnitude of γ, the frequency of vibration of the bond which is breaking.[42] For an infra red wave length of 3μ this would have very approximately a frequency of 10^5 A.

In the foregoing discussion we have not given any consideration to the possible effect of steric hindrance which has already been discussed to some extent (pp. 70, 81). The reaction (1) $CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_4 + CH_3CH_2CH_2CH_2$ — involves the making and breaking of a C — H bond, whereas the reaction (2) $CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_3 + CH_3CH_2CH_2$ — involves the making and breaking of the much weaker C — C bond; it is not unreasonable therefore on this basis to infer that the reaction involving the breaking of the carbon skeleton proceeds with a lower activation energy[43] than the reaction involving merely the removal of a hydrogen atom. However in view of the experimental evidence available we are forced to conclude that the presence of a steric factor diminishes to negligible proportions the the rate of the reaction causing rupture of the carbon skeleton, as compared with the rate of the reaction involving the removal of hydrogen atoms. Assuming that the reaction between a methyl group and a butane molecule to remove a hydrogen atom requires an activation energy of 16 Cal., reaction occurs at 600° C., after approximately 10^4 collisions; if we assume that the skeleton breaking reaction requires only 12 Cal., this reaction occurs at 600° C. after 10^3 collisions. Consequently we must assume a steric factor in reaction (1) which has a minimum value of 10^3 in order to make it negligible in comparison with the reaction (2).

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[39] Some recent results of Allen and Sickman, *J. Am. Chem. Soc.*, 56, 2031 (1934) indicate that the decomposition of acetaldehyde should be inhibited by packing the reaction vessel if the decomposition proceeds through a chain mechanism.

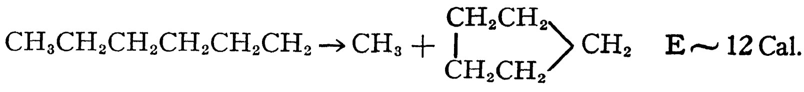
[40] Rice and Glasebrook, *J. Am. Chem. Soc.*, 56, 741 (1934).

[41] See Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., 1932.

[42] See Herzfeld, *Ann. Phys.*, 59, 635 (1919); Dushman, *J. Am. Chem. Soc.*, 43, 397 (1921).

Moreover, although few experimental data on the decomposition of large molecules are available it seems plausible to assume two methods of decomposition for such a radical as *n*-hexyl; these may be represented by the equations:

$$CH_3CH_2CH_2CH_2CH_2CH_2 \rightarrow CH_3CH_2CH_2CH_2 + C_2H_4 \quad E \sim 30\text{ Cal.}$$



$$CH_3CH_2CH_2CH_2CH_2CH_2 \rightarrow CH_3 + \begin{matrix} CH_2CH_2 \\ | \\ CH_2CH_2 \end{matrix}\!\!\!\!>CH_2 \quad E \sim 12\text{ Cal.}$$

If we assume values of 30 and 12 Cal. respectively for the activation energies of these reactions, a steric factor of 10^{-6} in the rate expression would be required to make the second reaction negligible at 650° C.; on the other hand even with this steric factor, the second reaction would predominate at 300° C. because the steric factor is not dependent on

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[48] The steric effect discussed in this and the following paragraph may be dependent to a greater or less extent on temperature. This would be the case if the screening effect on a C — C bond of the attached atoms or groups, can be overcome by a colliding particle possessing high kinetic energy which pushes aside the hindering substituents and causes a stretching of the C — C bond. This effect is discussed in another connection by W. Hückel, *Chem. Zeit.*, 58, 813 (1934).

temperature;[43] this behaviour is illustrated in Fig. 14. It will be seen that steric hindrance may bring about two entirely different methods of decomposition of large radicals depending on the temperature at which decomposition occurs.

Pattern Reactions.—The kinetics of the decompositions of the organic molecules ethane, acetone, dimethyl ether and acetaldehyde have been worked out in detail[17] according to the free radical mechanism illustrated in the following chapters. In all cases there is a primary rupture of the molecule (usually at a C–C bond) producing two free radicals which then react with the surrounding molecules and initiate chains in which certain radicals, called carriers, are continuously regenerated; eventually the carriers collide with each other and the chain is broken.

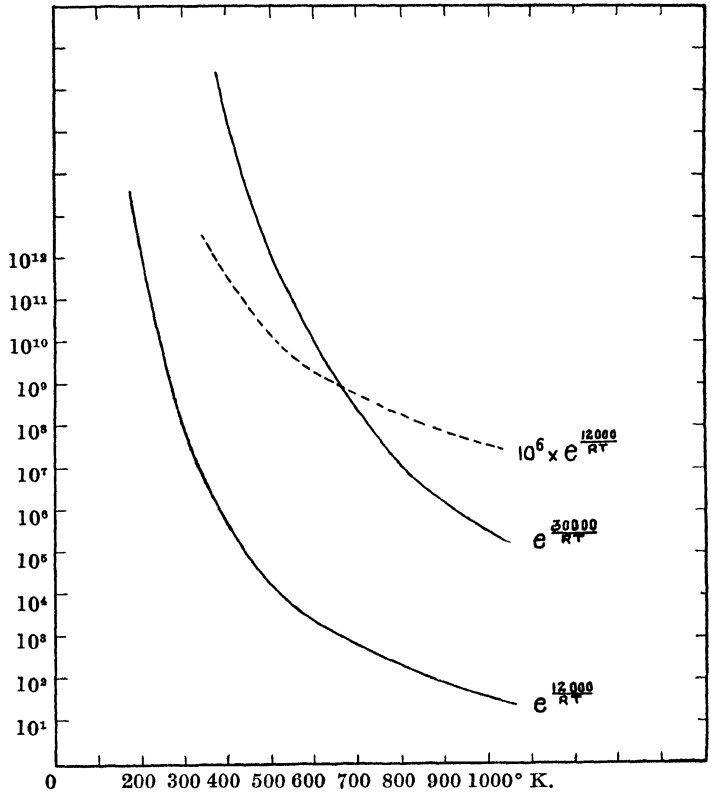

FIG. 14.—Effect of steric hindrance on reaction rate.

When one writes down all the possible reactions the mechanism is extremely complicated, but detailed examination[17] has shown that only very few of the reactions are important and that the rest may be safely neglected. For molecules that contain only one kind of hydrogen atom (and which have therefore only one chain cycle) the only important reactions are those involving the primary rupture of the substrate molecule into two free radicals, the two reactions of the chain cycle and the final collision of the chain carriers to produce one or more molecules. These may be represented as follows:[43a]

				E (Cal.)
(1)	$M_1 \rightarrow R_1 + M_2$	k_1	E_1	80
(2)	$R_1 + M_1 \rightarrow R_1H + R_2$	k_2	E_2	15
(3)	$R_2 \rightarrow R_1 + M_3$	k_3	E_3	38
(4)	$R_1 + R_2 \rightarrow M_4$	k_4	E_4	8.

A molecule M_1 decomposes into a radical R_1 and a smaller molecule. The radical R_1 picks off a hydrogen atom from M_1 forming the molecule R_1H and the radical R_2, which in turn decomposes into the molecule M_3 and regenerates radical R_1. The chain terminates by collision of R_1 and R_2. In the following rate equations the letters representing the substances are also used to represent concentrations:

$$\frac{dR_1}{dt} = 0 = k_1M_1 - k_2R_1M_1 + k_3R_2 - k_4R_1R_2$$

$$\frac{dR_2}{dt} = 0 = k_2R_1M_1 - k_3R_2 - k_4R_1R_2$$

These equations apply necessarily only to the very early stages of the reaction after the stationary state has been reached. Solving for R_1 and R_2 gives approximately:[43b]

$$R_1 = \sqrt{\frac{2\,k_2k_4}{k_1k_3}}\,; \qquad R_2 = M_1\sqrt{\frac{k_1k_2}{2\,k_3k_4}}$$

[43a] Other pattern reactions, in which M_1 dissociates into more than one radical, (which may or may not be identical with R_1) yield the same result except for a small factor in the chain length. Recombination of two of the small radicals R_1 is prevented in this scheme by assigning values of E for the two chain reactions such that the concentration of R_2 is high compared with R_1. The compound $R_2 - R_2$ formed by combination of two of the large radicals R_2 is supposed to be unstable as compared with the substrate M_1 and dissociates easily into the radical R_2.

[43b] The error is about the size of ± $1/n$ where n = chain length.

The overall rate of decomposition of M_1 is given by

$$-\frac{dM_1}{dt} = k_1M_1 + k_2R_1M_1 = k_1M_1\left(1 + \frac{k_2}{k_1}\sqrt{\frac{k_1k_3}{2\,k_2k_4}}\right)$$
$$= k_1M_1\left(1 + \sqrt{\frac{k_2k_3}{2\,k_1k_4}}\right) \sim M_1\sqrt{\frac{k_1k_2k_3}{2\,k_4}}$$

that is, it follows a unimolecular law. The overall rate of reaction is determined by two factors, the rate of the primary reaction (k_1M_1) and that of the chain reaction ($k_2R_1M_1$); the ratio k_2R_1/k_1 of these two rates gives the length of the chain.[44] We have then:

$$\frac{k_2}{k_1}R_1 = \frac{k_2}{k_1}\sqrt{\frac{k_1k_3}{2\,k_2k_4}} = \sqrt{\frac{k_2k_3}{2\,k_1k_4}}$$
$$\sim e^{(E_1+E_4-E_2-E_3)/2RT}.$$

It is of interest to calculate the concentration of methyl radicals (radical R_1) present in acetone at 600° C. This is given by the expression [34]

$$\sqrt{\frac{k_1k_3}{2\,k_2k_4}} = 10^5 \times e^{-(E_1+E_3-E_2-E_4)/2RT}$$
$$= 10^5 \times 10^{-95/8.3} = 10^{-6.5}.$$

Since the unit of concentration is $10^{-1.38}$ moles per liter, approximately 10^{-8} moles of methyl groups are present per liter.

An attempt to test this experimentally[45] was made by allowing acetone vapor at 600° and 200 mm. to stream out through a small hole and pass over a cold tellurium mirror. No effect on the mirror was found even after two hours, during which time about 0.02 moles of acetone were caught in the liquid air trap. If we assume that the removal of 0.001 milligram of tellurium could be detected, this corresponds to approximately 10^{-8} moles. The 0.02 moles of acetone occupy approximately 1 l. under the conditions of the experiment and contain therefore approximately 10^{-8} moles of methyl groups; however, probably not more than 1–10% of the radicals leaving the furnace reach the mirror and the removal of 10^{-9}–10^{-10} moles of tellurium could probably not be detected with certainty.

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[44] The chain length may also be calculated with reference to the primary change plus the secondary changes that occur before the chain process starts. A small factor is then introduced depending on the number of the substrate molecules decomposed in processes prior to initiation of the chain.

[45] Rice, Rodowskas and Lewis, *J. Am. Chem. Soc.*, 56, 2497 (1934).

There is another method of decomposition of molecules that contain only one kind of hydrogen atom which differs from the scheme shown on p. 87 only in the chain terminating reaction.[45a] It may be represented as follows:

			E (Cal.)
(1)	$M_1 \rightarrow R_1 + M_2$	k_1 E_1	70
(2)	$R_1 + M_1 \rightarrow R_1H + R_2$	k_2 E_2	15
(3)	$R_2 \rightarrow R_1 + M_3$	k_3 E_3	10
(5)	$2\,R_1 \rightarrow M_4$	k_4 E_4.	8

We have then:

$$\frac{\mathrm{d}R_1}{\mathrm{d}t} = 0 = k_1M_1 - k_2R_1M_1 + k_3R_2 - k_5R_1^2$$

$$\frac{\mathrm{d}R_2}{\mathrm{d}t} = 0 = k_2R_1M_1 - k_3R_2.$$

Solving for R_1 and R_2 gives approximately:

$$R_1 = \sqrt{\frac{M_1k_1}{k_5}}; \qquad R_2 = \frac{k_2}{k_3} M_1 \sqrt{\frac{M_1k_1}{k_5}}$$

The overall rate of decomposition of M_1 is given by,

$$-\frac{\mathrm{d}M_1}{\mathrm{d}t} = k_1M_1 + k_2R_1M_1 = k_1M_1 \left[1 + k_2\sqrt{\frac{M_1}{k_1k_5}}\,\right]$$

$$\sim M_1^{3/2}\, k_2 \sqrt{\frac{k_1}{k_5}}$$

The rate is therefore proportional to the 1.5 power of the concentration of the substrate molecule. The chain length is given as before by the ratio of $k_2R_1M_1$ to k_1M_1:

$$\frac{k_2R_1}{k_1} = \sqrt{M_1}\,\frac{k_2}{\sqrt{k_1k_5}}$$

but is no longer independent of the substrate concentration.

Similar schemes may be drawn up for more complicated molecules such as butane or diethyl ether which contain two kinds of hydrogen atoms and therefore should decompose through two chain cycles. If, however, the decomposition of these and similar substances really proceeds mainly through a chain it is necessary to exercise caution in comparing the results of such calculations with results obtained experimentally. The difficulty may be illustrated with reference to diethyl ether which, according to the chain mechanism (p. 115), should produce acetaldehyde as one of the decomposition products; the presence of acetaldehyde has also been proved experimentally.[46] It follows that the usual measurements of the rate of decomposition of diethyl ether are really measurements performed on mixtures with acetaldehyde and the two substances would not be expected to decompose independently since the radicals of the one enter into the decomposition of the other.[47] It seems somewhat probable that the decomposition of large molecules is in general extremely complicated owing to the participation of the products in the decomposition.

[45a] Whether the chain terminates by reaction (4) or reaction (5) depends on the values of E_1, E_2 and E_3.

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[46] Nef, *Ann.*, **318**, 198 (1901).

[47] Furthermore the method of extrapolating back to the initial concentration (see O. K. Rice and Sickman, *J. Am. Chem. Soc.*, **56**, 1444 (1934)) will not give the true initial rate of decomposition of the pure substrate unless the products have no influence on its rate of decomposition.

CHAPTER VII

PARAFFIN HYDROCARBONS

It is natural to consider the decomposition of the paraffin hydrocarbons first since, having only two kinds of bonds, they are the simplest class of organic compound. In this chapter we have calculated the products formed in the decomposition of the various paraffin hydrocarbons at 600° C., on the assumption [1] that at this temperature the relative chances of reaction of primary, secondary, and tertiary hydrogen atoms are in the ratio 1 : 2 : 10; this corresponds to a diminution of activation energy of 1200 and 4000 cal. respectively for the reaction of the radicals with secondary and tertiary hydrogen atoms.

Methane.—The decomposition of methane has been recently studied by Kassel,[1a] by Storch [2] and by Belchetz.[3] All of these investigators have adopted a mechanism based on Nef's idea of bivalent carbon; [4] the scheme suggested by Kassel [1a] consists of the two reactions,

$$CH_4 \rightarrow CH_2 + H_2$$
$$CH_2 + CH_4 \rightarrow C_2H_6$$

followed by successive dehydrogenation steps. However, work in this laboratory on the decomposition of methane in a flowing system at low pressures [5] has shown that the fragments leaving the furnace are methyl groups since dimethyl ditelluride $CH_3TeTeCH_3$ is formed and no telluroformaldehyde $(HCHTe)_n$ can be identified. It is of course possible [6] that a primary dissociation into a hydrogen molecule and the methylene group may be followed by the reaction,

$$CH_2 + CH_4 \rightarrow 2\,CH_3;$$

but on the basis of the work done so far the mechanism of the methane decomposition seems to be uncertain.

Ethane.—According to the free radical mechanism the primary decomposition of ethane produces two methyl groups by rupture of the C—C bond. These radicals then react with the surrounding ethane molecules to form methane and ethyl groups, which latter finally decompose into ethylene and atomic hydrogen. Designating the primary rupture by P, the secondary reaction by S, and the chain reaction by A we have:[7]

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[1] Rice, *J. Am. Chem. Soc.*, **53**, 1959 (1931).

[1a] Kassel, *J. Am. Chem. Soc.*, **54**, 3949 (1932).

[2] Storch, *ibid.*, **54**, 4188 (1932).

[3] Belchetz, *Trans. Far. Soc.*, **34**, 170 (1934).

[4] Nef, *Ann.*, **298**, 202 (1897).

[5] Rice and Dooley, *J. Am. Chem. Soc.*, **56**, 2747 (1934). The results of this work are not in agreement with those of Belchetz, see ref. (3).

[6] Rice, *Trans. Far. Soc.*, **34**, 247 (1934).

$$\begin{array}{ll} \mathrm{P} & C_2H_6 \rightarrow 2\,CH_3 \\ \mathrm{S} & CH_3 + C_2H_6 \rightarrow CH_4 + CH_3CH_2 \\ \mathrm{A} & C_2H_6 + R \rightarrow RH + CH_3CH_2 \rightarrow RH + C_2H_4 + H. \\ & \qquad\qquad R = H. \end{array}$$

The decomposition of ethane is particularly simple because, since there is only one type of C—H bond in the molecule, there can be only one chain cycle, which will produce hydrogen and ethylene in equal amounts; so far as the chain cycle is concerned the decomposition of ethane should produce these two substances only. The termination of the chain is caused by collision between the ethyl groups and the hydrogen atoms to give either ethane or hydrogen and ethylene.[8] The length of the chain has been calculated to be about 100 cycles,[8] which is in approximate agreement with the experimental fact that 2% of methane is present.

Propane.—The primary decomposition of propane yields methyl and ethyl radicals by rupture of a C—C bond. The mechanism may be represented as follows:

$$\begin{array}{llll} \mathrm{P_1} & C_3H_8 & & \rightarrow CH_3 + CH_3CH_2 \\ \mathrm{S_1} & CH_3CH_2 + C_3H_8 & & \rightarrow C_2H_6 + CH_3CH_2CH_2 \text{ or} \\ \mathrm{S_2} & CH_3CH_2 + C_3H_8 & & \rightarrow C_2H_6 + CH_3CHCH_3 \\ \mathrm{A_1} & C_3H_8 & + R & \rightarrow RH + CH_3CH_2CH_2 \\ & & & \rightarrow RH + C_2H_4 + CH_3 \\ \mathrm{A_2} & C_3H_8 & + R & \rightarrow RH + CH_3CHCH_3 \\ & & & \rightarrow RH + CH_3CH{=}CH_2 + H \\ & & R = CH_3, H. & \end{array}$$

The main products of the reaction are governed by the chain mechanism, and consist therefore of methane and ethylene in equal amounts, and of hydrogen and propylene, also in equal amounts. Since there are six primary and two secondary hydrogen atoms (which are twice as reactive as the primary) we may summarize the result quantitatively as follows:

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[7] This terminology will be used throughout this and the subsequent chapters.

[8] Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

$$A_1 \quad 6\,C_3H_8 \rightarrow 6\,CH_4 + 6\,C_2H_4$$

$$A_2 \quad 4\,C_3H_8 \rightarrow 4\,C_3H_6 + 4\,H_2.$$

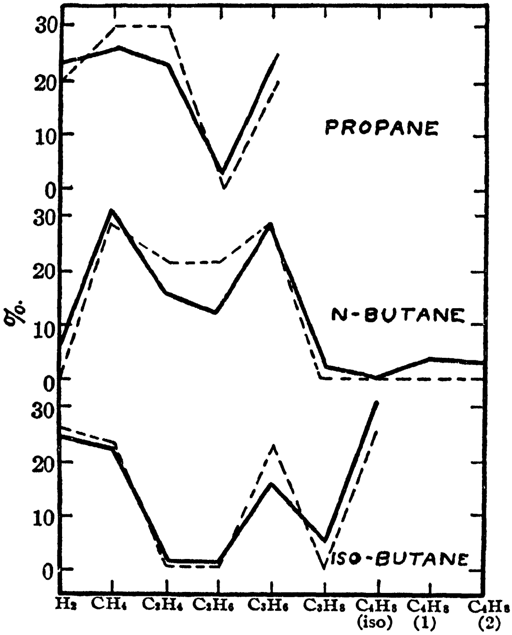

FIG. 15.—Observed (—) and calculated (- - - -) products in the thermal decomposition of hydrocarbons.

In this case the chain cycles are terminated by collisions between the various radicals taking part in the chain reaction. It does not seem possible as yet to determine which of the reactions between these radicals is mainly responsible for breaking the chain. However, by analogy with ethane, dimethyl ether, and acetone we may infer that the chain is most frequently terminated by reactions between the carriers and propyl or isopropyl radicals. With chains about 100 cycles long we should therefore expect to find a small quantity of the butanes, together with some ethane[9] formed in reactions S_1 and S_2.

Isobutane.—The decomposition of isobutane may be represented as follows:

$$\begin{aligned}
&P_1 \quad C_4H_{10} \rightarrow CH_3 + CH_3CHCH_3 \\
&S_1 \quad CH_3CHCH_3 \rightarrow C_3H_6 + H \\
&A_1 \quad C_4H_{10} + R \rightarrow RH + (CH_3)_2CHCH_2 \\
&\qquad\qquad\qquad \rightarrow RH + C_3H_6 + CH_3 \\
&A_2 \quad C_4H_{10} + R \rightarrow RH + (CH_3)_3C \\
&\qquad\qquad\qquad \rightarrow RH + (CH_3)_2C{=}CH_2 + H \\
&\qquad\qquad\quad R = CH_3, H.
\end{aligned}$$

The main products of the reaction will be methane and propylene in equal amounts plus hydrogen and isobutylene also in equal amounts. The quantitative decomposition may be summarized in the same manner as before:

$$\begin{aligned}
&A_1 \quad 9\,C_4H_{10} \rightarrow 9\,CH_4 + 9\,C_3H_6 \\
&A_2 \quad 10\,C_4H_{10} \rightarrow 10\,C_4H_8(\text{iso}) + 10\,H_2.
\end{aligned}$$

We may also assume, as before, that the termination of the chain occurs chiefly by collision of the carriers CH_3 and H with the radicals $(CH_3)_3C$ and $(CH_3)_2CHCH_2$. We should then expect to find small quantities of neopentane and isopentane among the products. However, ethane has been reported as being the only substance present in small quantity[10] which would indicate that the chain breaks by collision of methyl groups.

n-Butane.—The decomposition of butane may be represented as follows:

$$\begin{aligned}
&P_1 \quad C_4H_{10} \rightarrow CH_3 + CH_3CH_2CH_2 \\
&P_2 \quad C_4H_{10} \rightarrow 2\,CH_3CH_2 \\
&S_1 \quad CH_3CH_2CH_2 \rightarrow C_2H_4 + CH_3 \\
&A_1 \quad C_4H_{10} + R \rightarrow RH + CH_3CH_2CH_2CH_2 \\
&\qquad\qquad\qquad \rightarrow RH + C_2H_4 + CH_3CH_2
\end{aligned}$$

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[9] See Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).
[10] Marek and Neuhaus, *Ind. Eng. Chem.*, **25**, 516 (1933).

$$A_2 \quad C_4H_{10} + R \rightarrow RH + CH_3CH_2CH\,CH_3$$
$$\rightarrow RH + C_3H_6 + CH_3$$
$$R = CH_3, CH_3CH_2.$$

The reaction may then be summarized as follows:

$$A_1 \quad 6\,C_4H_{10} \rightarrow 6\,C_2H_4 + 6\,C_2H_6$$
$$A_2 \quad 8\,C_4H_{10} \rightarrow 8\,C_3H_6 + 8\,CH_4$$

Termination of the chains presumably will result in small quantities of pentanes, hexanes, and propane. Neuhaus and Marek,[11] who investigated this decomposition very carefully, apparently found about 1% of propane present, as well as appreciable quantities of hydrogen, butene-1 and butene-2, which indicates that the reaction involving direct separation of molecular hydrogen is occurring as well as the chain.

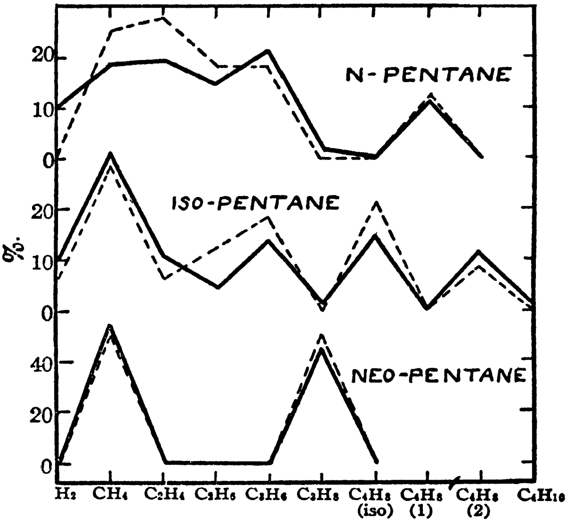


FIG. 16.—Observed (—) and calculated (- - - -) products in the thermal decomposition of the pentanes.

n-Pentane.—For this and the following paraffin hydrocarbons we will omit the primary and secondary reactions, because they are not of importance in connection with the final products. The chain mechanism is:

---

[11] Neuhaus and Marek, *Ind. Eng. Chem.*, **24**, 400 (1932).

$$\begin{aligned}
A_1 \quad C_5H_{12} + R &\rightarrow RH + CH_3CH_2CH_2CH_2CH_2 \\
&\rightarrow RH + C_2H_4 + CH_3CH_2CH_2 \\
&\rightarrow RH + C_2H_4 + C_2H_4 + CH_3
\end{aligned}$$

$$\begin{aligned}
A_2 \quad C_5H_{12} + R &\rightarrow RH + CH_3CHCH_2CH_2CH_3 \\
&\rightarrow RH + C_3H_6 + CH_3CH_2
\end{aligned}$$

$$\begin{aligned}
A_3 \quad C_5H_{12} + R &\rightarrow RH + CH_3CH_2CHCH_2CH_3 \\
&\rightarrow RH + C_4H_8\text{—}1 + CH_3
\end{aligned}$$

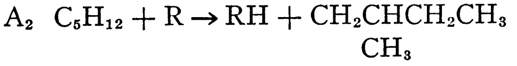
$$R = CH_3, CH_3CH_2.$$

Thus there are three chain cycles which may be summarized as follows:

$$\begin{aligned}
&A_1 \quad 6\,C_5H_{12} \rightarrow 12\,C_2H_4 + 6\,CH_4 \\
&A_2 \quad 8\,C_5H_{12} \rightarrow 8\,C_3H_6 + 8\,C_2H_6 \\
&A_3 \quad 4\,C_5H_{12} \rightarrow 4C_4H_8\text{—}1 + 4\,CH_4
\end{aligned}$$

Iso-pentane.—The chain reactions are:

$$\begin{aligned}
A_1 \quad C_5H_{12} + R &\rightarrow RH + (CH_3)_2CHCH_2CH_2 \\
&\rightarrow RH + C_2H_4 + CH_3CHCH_3 \\
&\rightarrow RH + C_2H_4 + C_3H_6 + H
\end{aligned}$$



$$A_2 \quad C_5H_{12} + R \rightarrow RH + \underset{\displaystyle CH_3}{CH_2CHCH_2CH_3}$$

$$\begin{aligned}
&\rightarrow RH + C_3H_6 + CH_3CH_2 \\
\text{or} \qquad &\rightarrow RH + C_4H_8\text{—}1 + CH_3
\end{aligned}$$

$$\begin{aligned}
A_3 \quad C_5H_{12} + R &\rightarrow RH + (CH_3)_2CHCHCH_3 \\
&\rightarrow RH + C_4H_8\text{—}2 + CH_3
\end{aligned}$$

$$\begin{aligned}
A_4 \quad C_5H_{12} + R &\rightarrow RH + (CH_3)_2CCH_2CH_3 \\
&\rightarrow RH + C_4H_8(\text{iso}) + CH_3
\end{aligned}$$

$$R = H, CH_3, CH_3CH_2.$$

In the cycle A_2 the large radical originally formed can decompose in either of two ways; in the following summary we assume equal probabilities for these two reactions:

$$\begin{aligned}
&A_1 \quad 3\,C_5H_{12} \rightarrow 3\,C_2H_4 + 3\,C_3H_6 + 3\,H_2 \\
&A_2 \quad 6\,C_5H_{12} \rightarrow 3\,C_3H_6 + 3\,C_2H_6 + 3\,C_4H_8\text{—}1 + 3\,CH_4 \\
&A_3 \quad 4\,C_5H_{12} \rightarrow 4\,C_4H_8\text{—}2 + 4\,CH_4 \\
&A_4 \quad 10\,C_5H_{12} \rightarrow 10\,C_4H_8(\text{iso}) + 10\,CH_4
\end{aligned}$$

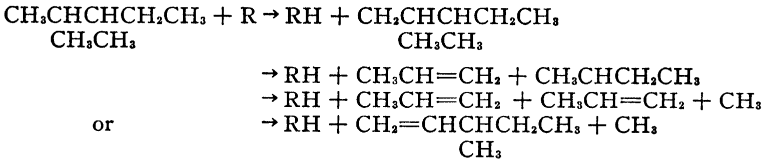
Neo-pentane.—The only chain reaction is:

$$\begin{aligned} A\quad C_5H_{12} + R &\rightarrow RH + (CH_3)_3CCH_2 \\ &\rightarrow RH + C_4H_8(\text{iso}) + CH_3 \\ R &= CH_3. \end{aligned}$$

Therefore neo-pentane should yield an equimolecular mixture of methane and isobutylene as the principal products of its decomposition.

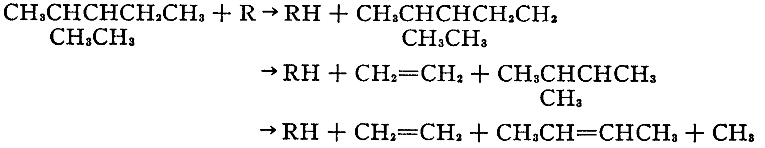
2, 3-Dimethyl pentane.—To represent the decomposition of this hydrocarbon requires six chain cycles. It is more complicated than is usual even for large molecules and we give it merely as an example, to show that the treatment for simpler molecules can be applied in exactly the same manner to more complicated molecules.

A_1



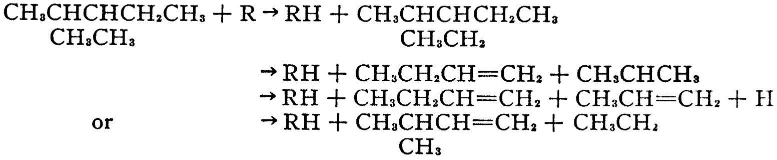
$$\begin{aligned} CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R &\rightarrow RH + CH_2\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 \\ &\rightarrow RH + CH_3CH{=}CH_2 + CH_3CHCH_2CH_3 \\ &\rightarrow RH + CH_3CH{=}CH_2 + CH_3CH{=}CH_2 + CH_3 \\ \text{or}\qquad &\rightarrow RH + CH_2{=}CH\underset{CH_3}{CH}CH_2CH_3 + CH_3 \end{aligned}$$

A_2



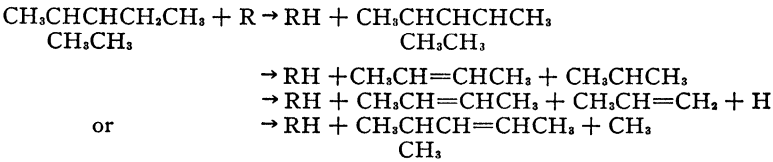
$$\begin{aligned} CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R &\rightarrow RH + CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_2 \\ &\rightarrow RH + CH_2{=}CH_2 + CH_3\underset{CH_3}{CH}CHCH_3 \\ &\rightarrow RH + CH_2{=}CH_2 + CH_3CH{=}CHCH_3 + CH_3 \end{aligned}$$

A_3



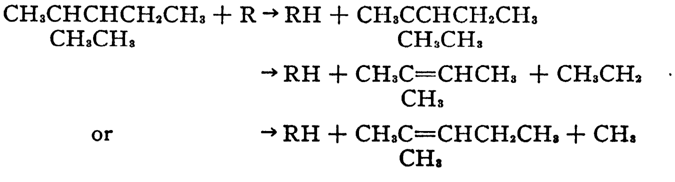
$$\begin{aligned} CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R &\rightarrow RH + CH_3\underset{CH_3}{CH}\underset{CH_2}{CH}CH_2CH_3 \\ &\rightarrow RH + CH_3CH_2CH{=}CH_2 + CH_3CHCH_3 \\ &\rightarrow RH + CH_3CH_2CH{=}CH_2 + CH_3CH{=}CH_2 + H \\ \text{or}\qquad &\rightarrow RH + CH_3\underset{CH_3}{CH}CH{=}CH_2 + CH_3CH_2 \end{aligned}$$

A_4

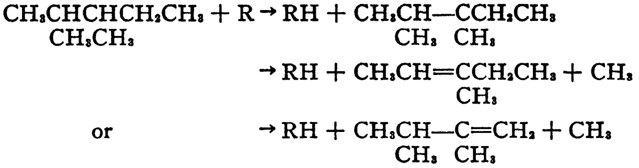


$$\begin{aligned} CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R &\rightarrow RH + CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CHCH_3 \\ &\rightarrow RH + CH_3CH{=}CHCH_3 + CH_3CHCH_3 \\ &\rightarrow RH + CH_3CH{=}CHCH_3 + CH_3CH{=}CH_2 + H \\ \text{or}\qquad &\rightarrow RH + CH_3\underset{CH_3}{CH}CH{=}CHCH_3 + CH_3 \end{aligned}$$

A_5

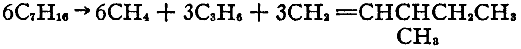


$$\begin{aligned} CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R &\rightarrow RH + CH_3\underset{CH_3}{C}\underset{CH_3}{CH}CH_2CH_3 \\ &\rightarrow RH + CH_3\underset{CH_3}{C}{=}CHCH_3 + CH_3CH_2 \\ \text{or}\qquad &\rightarrow RH + CH_3\underset{CH_3}{C}{=}CHCH_2CH_3 + CH_3 \end{aligned}$$

A₆ 

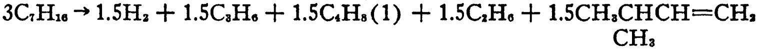
$$CH_3\underset{CH_3}{CH}\underset{CH_3}{CH}CH_2CH_3 + R \rightarrow RH + CH_3\underset{CH_3}{CH}{-}\underset{CH_3}{C}CH_2CH_3$$
$$\rightarrow RH + CH_3CH{=}\underset{CH_3}{C}CH_2CH_3 + CH_3$$
$$\text{or} \qquad \rightarrow RH + CH_3\underset{CH_3}{CH}{-}\underset{CH_3}{C}{=}CH_2 + CH_3$$

In A_1, A_3, A_4, A_5 and A_6 the radical first produced can decompose into an olefin and a smaller radical in either of two ways by rupture of a C—C bond; it seems logical to assume equal probabilities for the two dissociations in each case. The decomposition can then be summarized as follows:

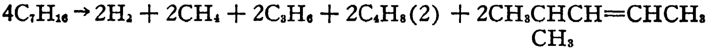
A₁ 

$$6C_7H_{16} \rightarrow 6CH_4 + 3C_3H_6 + 3CH_2{=}CH\underset{CH_3}{CH}CH_2CH_3$$

A_2 $3C_7H_{16} \rightarrow 3CH_4 + 3C_2H_4 + 3C_4H_8(2)$

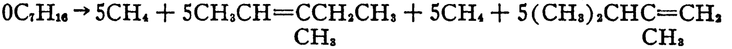
A₃ 

$$3C_7H_{16} \rightarrow 1.5H_2 + 1.5C_3H_6 + 1.5C_4H_8(1) + 1.5C_2H_6 + 1.5CH_3\underset{CH_3}{CH}CH{=}CH_2$$

A₄ 

$$4C_7H_{16} \rightarrow 2H_2 + 2CH_4 + 2C_3H_6 + 2C_4H_8(2) + 2CH_3\underset{CH_3}{CH}CH{=}CHCH_3$$

A_5 $10C_7H_{16} \rightarrow 5C_2H_6 + 5(CH_3)_2C{=}CHCH_3 + 5CH_4 + 5(CH_3)_2C{=}CHCH_2CH_3$

A₆ 

$$10C_7H_{16} \rightarrow 5CH_4 + 5CH_3CH{=}\underset{CH_3}{C}CH_2CH_3 + 5CH_4 + 5(CH_3)_2CH\underset{CH_3}{C}{=}CH_2$$

In Figs. 15 to 17 we show the calculated results for a number of paraffin hydrocarbons; whenever they were available we have included the experimental data[12] also. Considering the general character of the assumptions and the many approximations necessary, we consider the agreement between the calculated and experimental values satisfactory.

All the calculations made so far in this chapter concern decompositions carried out in the neighborhood of 600° and under approximately atmospheric pressure. We have assumed that under these conditions all free radicals with the exception of methyl and ethyl decompose. Obviously, however, the pressure under which the decomposition occurs will profoundly modify the reactions of the radicals. Diminution in pressure will favor their disintegration until finally at quite low pressures (perhaps less than 1 mm.) we may assume that only the stable methyl radical survives; methane should then be the only paraffin hydrocarbon among the products. At higher pressures we may expect to find the radicals reacting with the surrounding molecules to a greater or less extent, according to their stability; at atmospheric pressure both methyl and ethyl probably exist and consequently we find both methane and ethane among the products; at higher pressures we would expect methyl, ethyl, isopropyl and tert-butyl to react with the surrounding molecules; consequently, methane, ethane, propane and isobutane should appear in the products. Finally, at still higher pressures, all the radicals formed will react with the surrounding molecules to form saturated hydrocarbons.

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[12] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

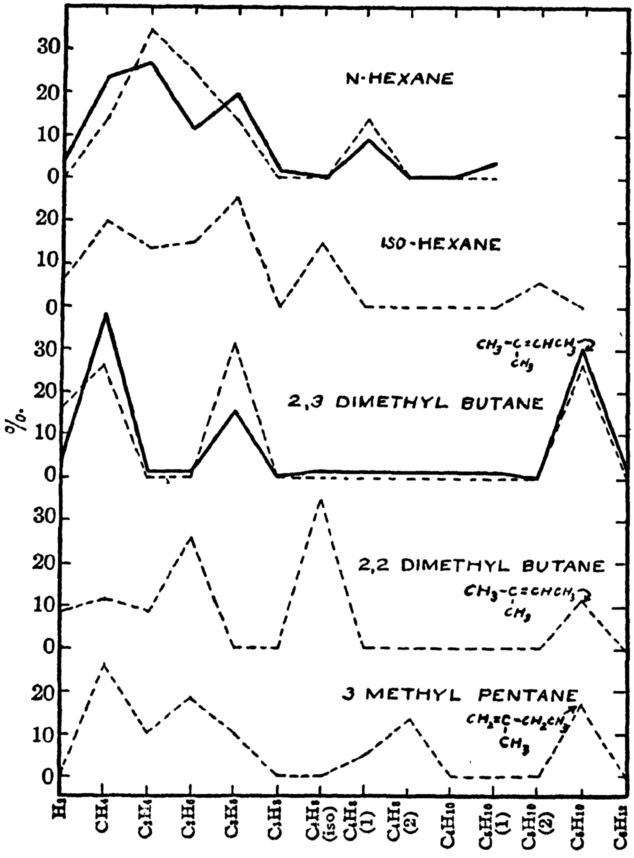


FIG. 17.—Observed (—) and calculated (- - - -) products in the thermal decomposition of the hexanes.

The foregoing argument refers to the effect of pressure changes at constant temperature and is based on the fact that the bimolecular reaction of the free radicals with the surrounding molecules is favored by increase of pressure whereas the unimolecular decomposition is unaffected. Thus when propane is decomposed at high pressures it should give mainly methane and ethylene; under these conditions isobutane should give chiefly methane and propylene. The calculated effect of pressure on the products of decomposition of pentane and isopentane are shown in Fig. 18.

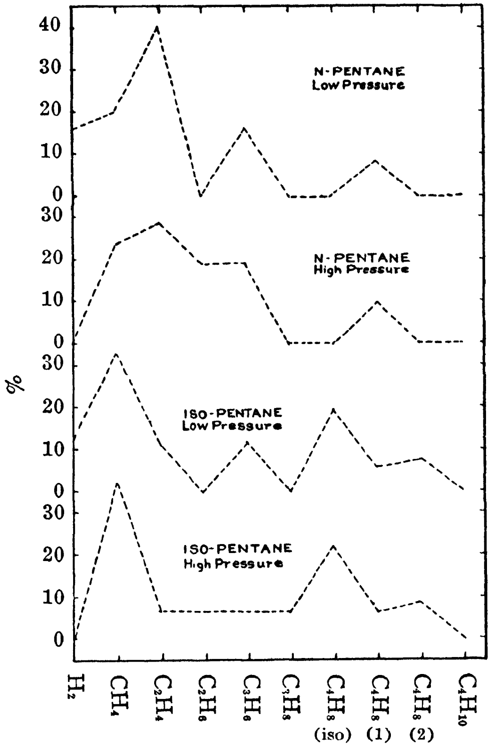


FIG. 18.—Calculated products in the thermal decomposition of hydrocarbons.

The temperature of decomposition also affects profoundly the relative amounts of products, especially if the hydrocarbon contains one or more tertiary atoms. The following relative rates for reactions of radicals with primary, secondary and tertiary hydrogen atoms[1] have been calculated for three different temperatures.

	Primary	Secondary	Tertiary
300°	1	3	33
600°	1	2.0	10.0
1000°	1	1.6	5

At high temperatures, differences in bond strength have a relatively small effect on the rate of reaction, whereas at low temperatures the more weakly bound hydrogen atoms react relatively much more readily.

There is a second effect brought about by change in temperature; a free radical such as ethyl produced in a chain cycle may either decompose to give ethylene and hydrogen atoms or it may react with the surrounding molecules to give ethane; since the activation energies of these two reactions will in general have different values, their relative rates will depend on temperature, high temperature favoring the reaction with the higher activation energy. The activation energy of the decomposition of the ethyl group has been taken[8] as 40 Cal. which is probably greater than the activation energy of its reaction with organic molecules; this is probably true also for the isopropyl and tertbutyl groups. We may assume then that at high temperatures these three groups mainly decompose, whereas at low temperatures they react with surrounding molecules. On the basis of these rules we have summarised the decomposition products for different hydrocarbons at high and low temperatures.

Propane.—The decomposition products at about 300° would be:

A_1 $6\,C_3H_8 \rightarrow 6\,CH_4 + 6\,C_2H_4$.

Since we assume that the isopropyl group is stable, the whole decomposition should proceed through the chain A_1.

Propane.—1000° C.

A_1 $6\,C_3H_8 \rightarrow 6\,CH_4 + 6\,C_2H_4$

A_2 $3.2\,C_3H_8 \rightarrow 3.2\,H_2 + 3.2\,C_3H_6$

Butane.—$CH_3CH_2CH_2CH_3$. 300° C.

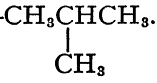
A_1 $6\,C_4H_{10} \rightarrow 6\,C_2H_4 + 6\,C_2H_6$

A_2 $12\,C_4H_{10} \rightarrow 12\,C_3H_6 + 12\,CH_4$

Butane.—1000° C.

A_1 $6\,C_4H_{10} \rightarrow 6\,C_2H_4 + 6\,C_2H_4 + 6\,H_2$

A_2 $6.4\,C_4H_{10} \rightarrow 6.4\,C_3H_6 + 6.4\,CH_4$

Isobutane.—

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$. 300° C.

A_1 $9\,C_4H_{10} \rightarrow 9\,CH_4 + 9\,C_3H_6$

Since we assume that the isobutyl group is stable, the whole decomposition should proceed through the chain A_1.

Isobutane.—1000° C.

A_1 $9\,C_4H_{10} \rightarrow 9\,CH_4 + 9\,C_3H_6$

A_2 $5\,C_4H_{10} \rightarrow 5\,H_2 + 5\,C_4H_8$(iso)

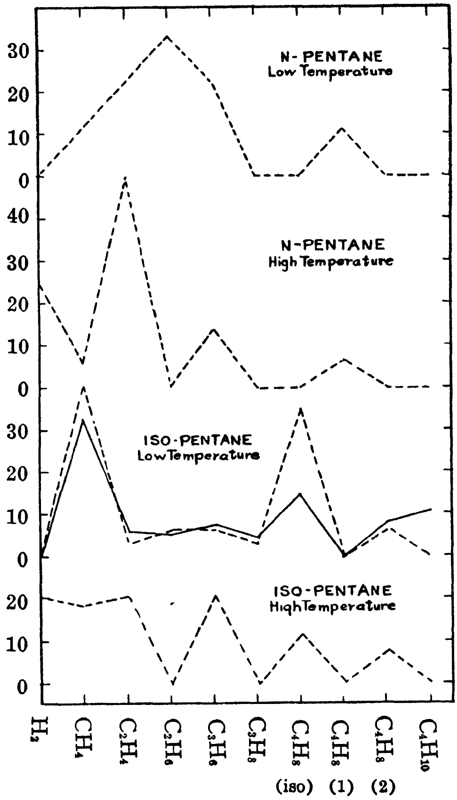


FIG. 19.—Observed (—) and calculated (- - - -) products in the thermal decomposition of hydrocarbons.

n-Pentane.—$CH_3CH_2CH_2CH_2CH_3$. 300° C.

A_1 $6\,C_5H_{12} \rightarrow 12\,C_2H_4 + 6\,CH_4$

A_2 $12\,C_5H_{12} \rightarrow 12\,C_3H_6 + 12\,C_2H_6$

A_3 $6\,C_5H_{12} \rightarrow 6\,C_4H_8(1) + 6\,CH_4$

n-Pentane.—1000° C.

A_1 $6\,C_5H_{12} \rightarrow 12\,C_2H_4 + 6\,CH_4$

A_2 $6.4\,C_5H_{12} \rightarrow 6.4\,C_3H_6 + 6.4\,C_2H_4 + 6.4\,H_2$

A_3 $3.2\,C_5H_{12} \rightarrow 3.2\,C_4H_8(1) + 3.2\,CH_4$

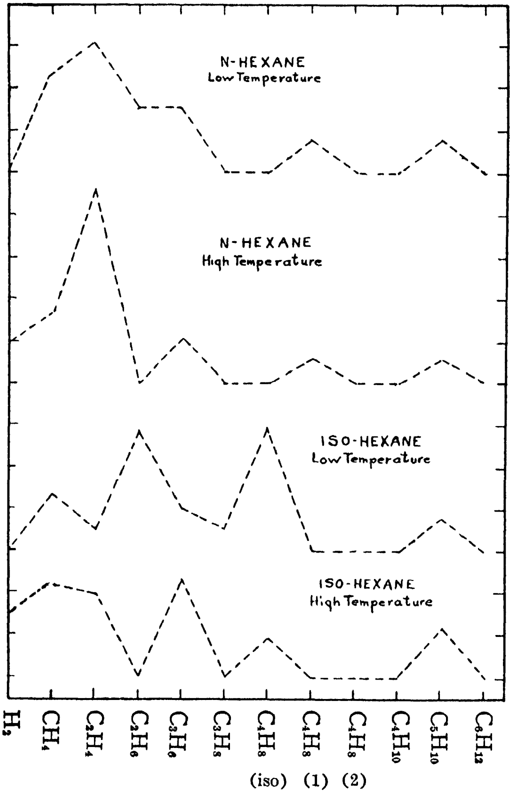
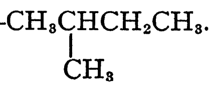


FIG. 20.—Calculated products in the thermal decomposition of hydrocarbons.

Isopentane.—



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3.$$

300° C.

A_1 $3\,C_5H_{12} \rightarrow 3\,C_2H_4 + 3\,C_3H_8$

A_2 $6\,C_5H_{12} \rightarrow 6\,C_3H_6 + 6\,C_2H_6$

A_3 $6\,C_5H_{12} \rightarrow 6\,C_4H_8(2) + 6\,CH_4$

A_4 $33\,C_5H_{12} \rightarrow 33\,C_4H_8(\text{iso}) + 33\,CH_4$

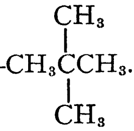
Isopentane.—1000° C.

A_1 $3\,C_5H_{12} \rightarrow 3\,C_2H_4 + 3\,C_3H_6 + 3\,H_2$

A_2 $6\,C_5H_{12} \rightarrow 6\,C_3H_6 + 6\,C_2H_4 + 6\,H_2$

A_3 $3.2\,C_5H_{12} \rightarrow 3.2\,C_4H_8(2) + 3.2\,CH_4$

A_4 $5\,C_5H_{12} \rightarrow 5\,C_4H_8(\text{iso}) + 5\,CH_4$

Neopentane.— $CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3$. This decomposition should result only in methane and isobutylene at all temperatures according to the chain reaction given on p. 97.

n-Hexane.—$CH_3CH_2CH_2CH_2CH_2CH_3$. 300° C.

A_1 $6\,C_6H_{14} \rightarrow 12\,C_2H_4 + 6\,C_2H_6$.

A_2 $12\,C_6H_{14} \rightarrow 12\,C_3H_6 + 12\,C_2H_4 + 12\,CH_4$

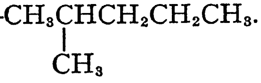
A_3 $12\,C_6H_{14} \rightarrow 6\,C_5H_{10}(1) + 6\,CH_4 + 6\,C_4H_8(1) + 6\,C_2H_6$

n-Hexane.—1000° C.

A_1 $6\,C_6H_{14} \rightarrow 12\,C_2H_4 + 6\,C_2H_4 + 6\,H_2$

A_2 $6.4\,C_6H_{14} \rightarrow 6.4\,C_3H_6 + 6.4\,C_2H_4 + 6.4\,CH_4$

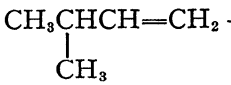
A_3 $6.4\,C_6H_{14} \rightarrow 3.2\,C_5H_{10}(1) + 3.2\,CH_4 + 3.2\,C_4H_8(1) + 3.2\,C_2H_4 + 3.2\,H_2$

Isohexane.— $CH_3\underset{CH_3}{C}HCH_2CH_2CH_3$. 300° C.

A_1 $3\,C_6H_{14} \rightarrow 3\,C_2H_4 + 3\,C_3H_6 + 3\,CH_4$

A_2 $6\,C_6H_{14} \rightarrow 3\,CH_4 + 3\,C_5H_{10}(1) + 3\,C_3H_6 + 3\,C_2H_4 + 3\,CH_4$

A_3 $6\,C_6H_{14} \rightarrow 6\,C_3H_6 + 6\,C_3H_8$



A_4 $6\,C_6H_{14} \rightarrow 3\,CH_4 + 3\,CH_3\underset{CH_3}{C}HCH{=}CH_2 + 3\,CH_4 + 3\,C_5H_{10}(2)$

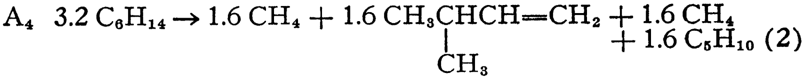
A_5 $33\,C_6H_{14} \rightarrow 33\,C_4H_8(\text{iso}) + 33\,C_2H_6$

Isohexane.—1000° C.

A_1 $3\,C_6H_{14} \rightarrow 3\,C_2H_4 + 3\,C_3H_6 + 3\,CH_4$

A_2 $6\,C_6H_{14} \rightarrow 3\,CH_4 + 3\,C_5H_{10}(1) + 3\,C_3H_6 + 3\,C_2H_4 + 3\,CH_4$

A$_3$ $3.2\,C_6H_{14} \rightarrow 3.2\,C_3H_6 + 3.2\,C_3H_6 + 3.2\,H_2$



A$_4$ $3.2\,C_6H_{14} \rightarrow 1.6\,CH_4 + 1.6\,CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CH_2 + 1.6\,CH_4 + 1.6\,C_5H_{10}$ (2)

A$_5$ $5\,C_6H_{14} \rightarrow 5\,C_4H_8(\text{iso}) + 5\,C_2H_4 + 5\,H_2$

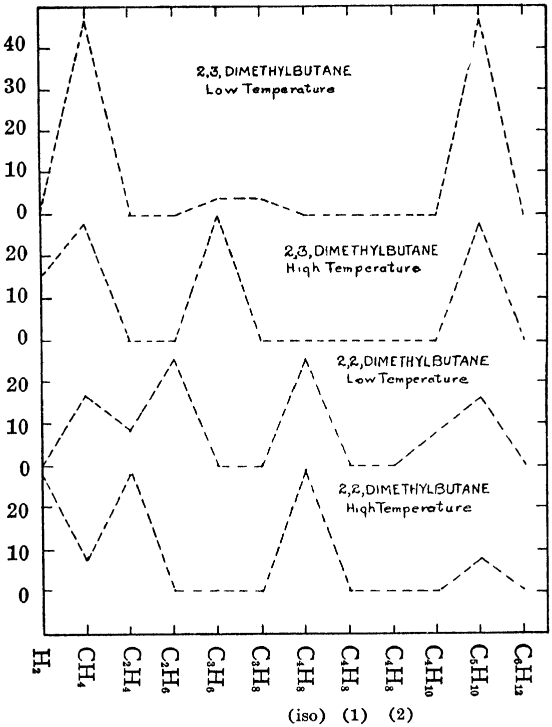
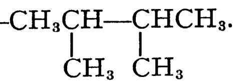


FIG. 21.—Calculated products in the thermal decomposition of hydrocarbons.



2, 3-Dimethylbutane.—$\underset{\displaystyle CH_3}{\underset{|}{CH_3CH}}\!-\!\underset{\displaystyle CH_3}{\underset{|}{CHCH_3}}$. 300° C.

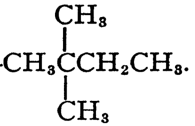
A$_1$ $12\,C_6H_{14} \rightarrow 6\,CH_4 + 6(CH_3)_2CH{=}CH_2 + 6\,C_3H_6 + 6\,C_3H_8$

A$_2$ $66\,C_6H_{14} \rightarrow 66\,CH_4 + 66(CH_3)_2C{=}CHCH_3$

2, 3-Dimethylbutane.—1000° C.

A$_1$ $12\,C_6H_{14} \rightarrow 6\,CH_4 + 6(CH_3)_2CHCH{=}CH_2 + 6\,C_3H_6 + 6\,C_3H_6 + 6\,H_2$

A$_2$ $10\,C_6H_{14} \rightarrow 5\,CH_4 + 5(CH_3)_2C{=}CHCH_3$

2, 2-Dimethylbutane.—
$CH_3C(CH_3)_2CH_2CH_3$. 300° C.

A₁ $3\ C_6H_{14} \rightarrow 3\ C_2H_4 + 3\ C_4H_{10}$(iso)

A₂ $9\ C_6H_{14} \rightarrow 9\ C_4H_8$(iso) $+ 9\ C_2H_6$

A₃ $6\ C_6H_{14} \rightarrow 6\ CH_4 + 6(CH_3)_2C{=}CHCH_3$

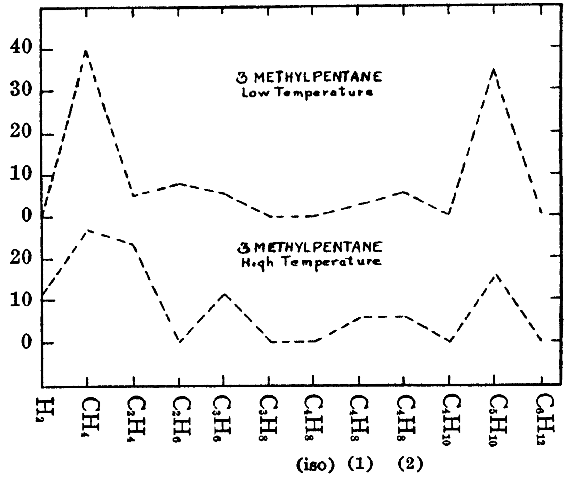


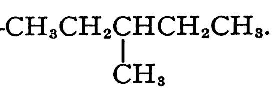
FIG. 22.—Calculated products in the thermal decomposition of hydrocarbons.

2, 2-Dimethylbutane.—1000° C.

A₁ $3\ C_6H_{14} \rightarrow 3\ C_2H_4 + 3\ C_4H_8$(iso) $+ 3\ H_2$

A₂ $9\ C_6H_{14} \rightarrow 9\ C_4H_8$(iso) $+ 9\ C_2H_4 + 9\ H_2$

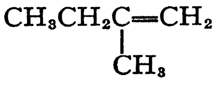
A₃ $3.2\ C_6H_{14} \rightarrow 3.2\ CH_4 + 3.2(CH_3)_2C{=}CHCH_3$

3-Methylpentane.—
$CH_3CH_2CH(CH_3)CH_2CH_3$. 300° C.

A₁ $3\ C_6H_{14} \rightarrow 3\ C_4H_8(1) + 3\ C_2H_6$

A₂ $6\ C_6H_{14} \rightarrow 6\ C_2H_4 + 6\ C_3H_6 + 6\ CH_4$

A₃ $12\ C_6H_{14} \rightarrow 6\ CH_4 + 6\ C_5H_{10}(2) + 6\ C_4H_8(2) + 6\ C_2H_6$

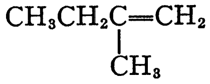
A₄ $33\ C_6H_{14} \rightarrow 33\ CH_4 + 33$ 
$CH_3CH_2C(CH_3){=}CH_2$

3-Methylpentane.—1000° C.

$A_1 \quad 3\,C_6H_{14} \rightarrow 3\,C_4H_8(1) + 3\,C_2H_4 + 3\,H_2$

$A_2 \quad 6\,C_6H_{14} \rightarrow 6\,C_2H_4 + 6\,C_3H_6 + 6\,CH_4$

$A_3 \quad 6.4\,C_6H_{14} \rightarrow 3.2\,CH_4 + 3.2\,C_5H_{10}(2) + 3.2\,C_4H_8(2)$
$\quad + 3.2\,C_2H_4 + 3.2\,H_2$



$A_4 \quad 5\,C_6H_{14} \rightarrow 5\,CH_4 + 5\,CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

The calculated results for some of the hydrocarbons are shown graphically in Fig. 19-22.

CHAPTER VIII

KETONES AND ALDEHYDES

The products formed in the thermal decomposition of ketones and aldehydes may be predicted exactly as in the case of the paraffin hydrocarbons. The course of the reactions is necessarily modified somewhat by the presence of the C=O group. Since this is a molecule of great stability and compared with CH_2 does not possess great chemical reactivity[1] we may assume that CO breaks off as a molecule whenever it occurs at the end of a free radical. In addition to such compounds as ethylene, propylene, and isobutylene we find among the decomposition products of ketones also the analogous compounds ketene, $CH_2=CO$, methyl ketene, $CH_3CH=CO$, and dimethyl ketene, $(CH_3)_2C=CO$.

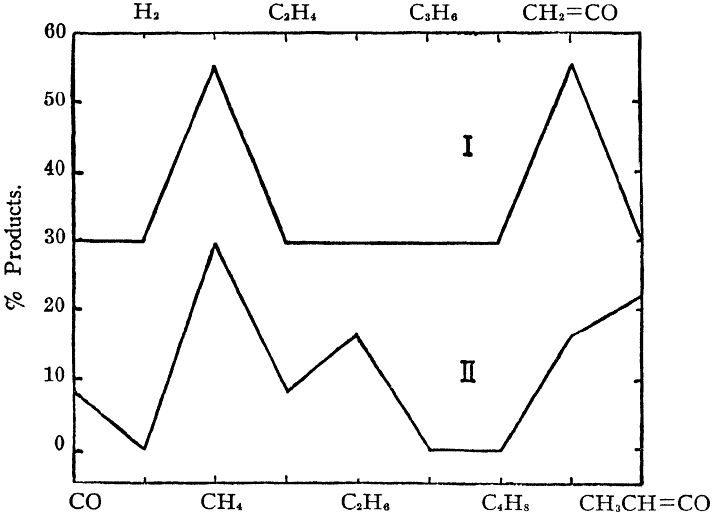


FIG. 23.—Calculated products in the thermal decomposition of acetone (I) and methyl ethyl ketone (II).

The CO group also has another effect in that it causes weakening of the C—H bonds in the α position. It is not possible at present to make an exact estimate of the extent of this influence; in the calculations in this chapter we have arbitrarily assumed that at 600° C. an α hydrogen atom has twice as much chance of reacting as has a corresponding hydrogen atom further removed from the CO group. This assumption, of course, affects only the quantitative composition of the products.

---

[1] See p. 18.

Acetone.—The primary decomposition may be represented as follows:

P_1 $CH_3COCH_3 \rightarrow CH_3 + CH_3CO$

S_1 $CH_3CO \rightarrow CO + CH_3$

A_1 $CH_3COCH_3 + R \rightarrow RH + CH_3COCH_2$
$RH + CH_2{=}CO + CH_3$
$R = CH_3$.

The radical CH_3COCH_2 decomposes by rupture of a C—C bond to give a free methyl radical and a very stable molecule, ketene, $CH_2{=}CO$ (the analogue of ethylene in the paraffin hydrocarbon decompositions); the free methyl group thus produced attacks one of the surrounding acetone molecules and continues the chain. The result of the decomposition produced by the chain cycle may then be written:

A_1 $CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO$

which is in excellent agreement with experimental studies.[2]

It has been predicted[3] that the chain ends by collision of the radical CH_3COCH_2 with CH_3 to give presumably methyl ethyl ketone; therefore a small quantity of this substance should be present, the exact amount depending on the length of the chain. This has not yet been tested experimentally.

Methyl Ethyl Ketone.—This decomposition is somewhat more complicated because there are three different kinds of C—H bonds. The chain mechanism may be represented as follows:

A_1 $CH_3COCH_2CH_3 + R \rightarrow RH + CH_3COCH_2CH_2$
$\rightarrow RH + C_2H_4 + CH_3CO$
$\rightarrow RH + C_2H_4 + CO + CH_3$

A_2 $CH_3COCH_2CH_3 + R \rightarrow RH + CH_2COCH_2CH_3$
$\rightarrow RH + CH_2{=}CO + CH_3CH_2$

---

[2] Vollrath, *Proc. Nat. Acad. Science*, **15**, 702 (1929); Weiler, Ph.D. Thesis, Johns Hopkins Univ., 1931; Waters, Ph.D. Thesis, Johns Hopkins Univ., 1932; Rice, Greenberg, Waters and Vollrath, *J. Am. Chem. Soc.*, **56**, 1760 (1934).

[3] Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

$$A_3\quad CH_3COCH_2CH_3 + R \rightarrow RH + CH_3COCHCH_3$$
$$\rightarrow RH + CH_3CH{=}CO + CH_3$$
$$R = CH_3,\ CH_3CH_2.$$

The products are therefore ethylene, methane, carbon monoxide, ketene,

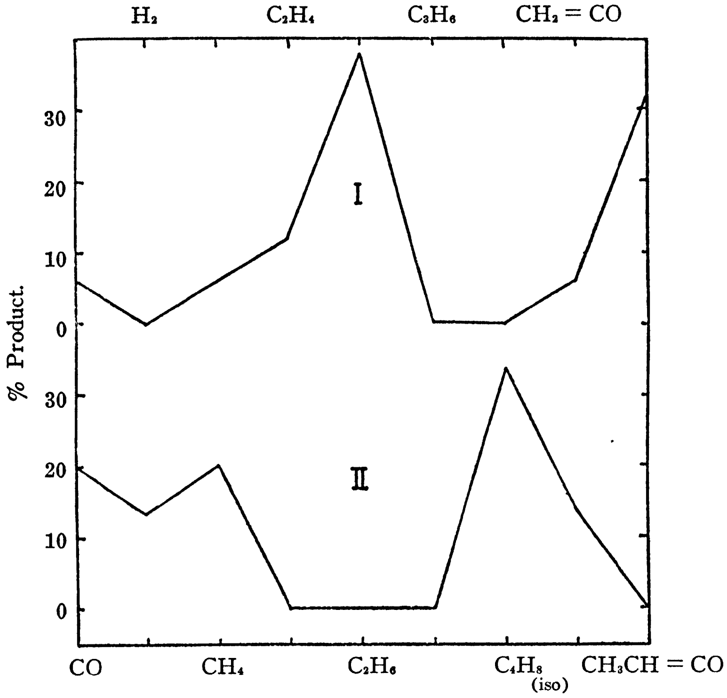


FIG. 24.—Calculated products in the thermal decomposition of diethyl ketone (I) and pinacolone (II).

ethane, and methyl ketene. The results may be summarized as follows, where K represents methyl ethyl ketone:

$$A_1\quad 3\,K \rightarrow 3\,C_2H_4 + 3\,CO + 3\,CH_4$$
$$A_2\quad 6\,K \rightarrow 6\,CH_2{=}CO + 6\,C_2H_6$$
$$A_3\quad 8\,K \rightarrow 8\,CH_3CH{=}CO + 8\,CH_4$$

Diethyl Ketone.—$CH_3CH_2COCH_2CH_3$. The chain reactions may be represented as follows:

$$\begin{aligned}
A_1 \quad C_5H_{10}O + R &\rightarrow RH + CH_3CH_2COCH_2CH_2 \\
&\rightarrow RH + C_2H_4 + CH_3CH_2CO \\
&\rightarrow RH + C_2H_4 + CO + CH_3CH_2 \\
\text{or} \qquad &\rightarrow RH + C_2H_4 + CH_2{=}CO + CH_3 \\
A_2 \quad C_5H_{10}O + R &\rightarrow RH + CH_3CHCOCH_2CH_3 \\
&\rightarrow RH + CH_3CH{=}CO + CH_3CH_2 \\
R &= CH_3, CH_3CH_2.
\end{aligned}$$

In the case of reaction A_1 the radical CH_3CH_2CO may decompose in either of two ways; in the following summary we have assumed equal probabilities for these decompositions.

$$A_1 \quad 6\,C_5H_{10}O \rightarrow 6\,C_2H_4 + 3\,CO + 3\,C_2H_6 + 3\,CH_2{=}CO + 3\,CH_4$$

$$A_2 \quad 16\,C_5H_{10}O \rightarrow 16\,CH_3CH{=}CO + 16\,C_2H_6$$

Methyl Propyl Ketone.—$CH_3COCH_2CH_2CH_3$. The chain reactions may be summarized as follows in exactly the same manner as in the previous examples:

$$A_1 \quad 3\,C_5H_{10}O \rightarrow 3\,C_2H_4 + 3\,CH_2{=}CO + 3\,CH_4$$

$$A_2 \quad 4\,C_5H_{10}O \rightarrow 4\,C_3H_6 + 4\,CO + 4\,CH_4$$

$$A_3 \quad 8\,C_5H_{10}O \rightarrow 8\,CH_3CH_2CH{=}CO + 8\,CH_4$$

$$A_4 \quad 6\,C_5H_{10}O \rightarrow 6\,C_2H_4 + 6\,CH_2{=}CO + 6\,CH_4$$

The products formed by reactions A_1 and A_4 in which a hydrogen atom is removed from each of the two end carbon atoms, chance to be the same in spite of the fact that the radicals formed in the two cases are different.

Methyl Isopropyl Ketone.—$CH_3COCH(CH_3)_2$. The decomposition of this ketone is interesting because according to the chain mechanism it should produce dimethylketene as well as ketene. The chain mechanism may be summarized as follows:

$$A_1 \quad 6\,C_5H_{10}O \rightarrow 6\,C_3H_6 + 6\,CO + 6\,CH_4$$

$$A_2 \quad 6\,C_5H_{10}O \rightarrow 6\,CH_2{=}CO + 6\,C_3H_6 + 6\,H_2$$

$$A_3 \quad 20\,C_5H_{10}O \rightarrow 20(CH_3)_2C{=}CO + 20\,CH_4$$

Pinacolone.—$CH_3COC(CH_3)_3$. The chain reaction for this ketone may be summarized as follows:

A $6\,C_6H_{12}O \rightarrow 6\,CH_2{=}CO + 6\,C_4H_8\text{—iso} + 6\,H_2$

A $9\,C_6H_{12}O \rightarrow 9\,C_4H_8(\text{iso}) + 9\,CO + 9\,CH_4$

These results for the different ketones are shown graphically in Figs. 23 and 24. Except for acetone no quantitative investigations appear to have been made.[4]

Acetaldehyde.—CH_3CHO. According to the theory of free radicals the decomposition of acetaldehyde and its homologues should proceed according to a very simple mechanism. If the assumption is made that the C — H bond of the aldehyde group is more than 6 Cal. weaker than the other C—H bonds in the molecule, it follows that no other hydrogen than that in the aldehyde group will enter into reaction. We would have then for acetaldehyde:

$$
\begin{array}{lll}
P_1 & CH_3CHO & \rightarrow CH_3 + HCO \\
S_1 & HCO & \rightarrow CO + H \\
S_2 & CH_3CHO + H & \rightarrow H_2 + CH_3CO \\
 & & \rightarrow H_2 + CO + CH_3 \\
A_1 & CH_3CHO + R & \rightarrow RH + CH_3CO \\
 & & \rightarrow RH + CO + CH_3 \\
 & & R = CH_3.
\end{array}
$$

There is therefore only one chain cycle and the products are carbon monoxide and methane produced in equal proportions.[5] It is also interesting to note that according to this mechanism the reaction should follow a 1.5 order [5d] which is in agreement with the experimental results of Fletcher and Hinshelwood.[5a]

Propionic Aldehyde.—CH_3CH_2CHO. The chain reaction is:

$$
\begin{array}{lll}
A & CH_3CH_2CHO + R & \rightarrow RH + CH_3CH_2CO \\
 & & \rightarrow RH + CO + CH_3CH_2 \\
 & \text{or} & \rightarrow RH + CH_2{=}CO + CH_3
\end{array}
$$

We do not know the relative probabilities of these two reactions.

---

[4] See Hurd, *Pyrolysis of Organic Compounds*, pp. 247-254. Chemical Catalog Co., 1929.

[5] (a) Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, **A 111**, 245 (1926); (b) Fletcher and Hinshelwood, *ibid.*, **141**, 41 (1933); (c) Kassel, *J. Phys. Chem.*, **34** 1166 (1930); (d) Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934); (e) Sickman and Allen, *ibid.*, **56**, 1251 (1934); (f) Leermakers, *ibid.*, **56**, 1537 (1934); (g) Allen and Sickman, *ibid.*, **56**, 2031 (1934).

Hinshelwood and Thompson,[6] who studied the kinetics of this decomposition, report methane, ethane, and carbon monoxide as the chief products.

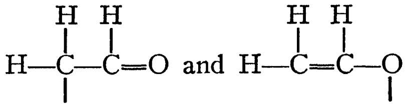
Some preliminary experiments on the decomposition of higher aldehydes[7] indicate that the aldehyde hydrogen atom is the most difficult to remove since no ketene was detected in the decomposition products of propionic or n-butyric aldehydes. Instead, acrolein seemed to be present as well as other products indicating in the case of butyric aldehyde the chain:

$$\begin{aligned} CH_3CH_2CH_2CHO + R &\rightarrow RH + CH_3CH_2CHCHO \\ &\rightarrow RH + CH_2{=}CHCHO + CH_3 \end{aligned}$$

Possibly the removal of an α–hydrogen atom occurs also in the decomposition of acetaldehyde,

$$CH_3CHO + R \rightarrow RH + {-}CH_2CHO$$

The radical —CH_2CHO may exist in the two forms:



$$H{-}\overset{H}{\underset{|}{\overset{|}{C}}}{-}\overset{H}{\overset{|}{C}}{=}O \quad \text{and} \quad H{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}\underset{|}{O}$$

Its decomposition into ketene and a hydrogen atom according to the equation,

$$CH_2CHO \rightarrow CH_2{=}CO + H$$

might then be expected to require a relatively high activation energy because of the resonance effect[8] in the CH_2CHO radical. Possibly also this radical may rearrange relatively easily according to the equation:

$$CH_2CHO \rightarrow CH_3CO$$

In either case, acetaldehyde might still be expected to decompose according to the mechanism given on p. 112.

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[6] Hinshelwood and Thompson, *Proc. Roy. Soc.*, **A 113**, 221 (1926).

[7] F. O. Rice and Donna Price, unpublished work.

[8] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); *idem.*, *J. Am. Chem. Soc.*, **18**, 293 (1932).

CHAPTER IX

ETHERS

The decomposition products of the ethers may also be predicted according to the foregoing rules; although there appear to be no quantitative experimental data of the relative proportions of the products formed in small fractional decompositions, it is nevertheless of interest to develop the theoretical mechanism for a few representative examples of this series of compounds. In calculating the results it has been assumed that the different C—H bonds in ethers have the same relative strengths as the corresponding bonds in paraffin hydrocarbons. It is probable, however, that the ether bond, —C—O—C—, somewhat affects the binding strengths of the hydrogen atoms α to it.

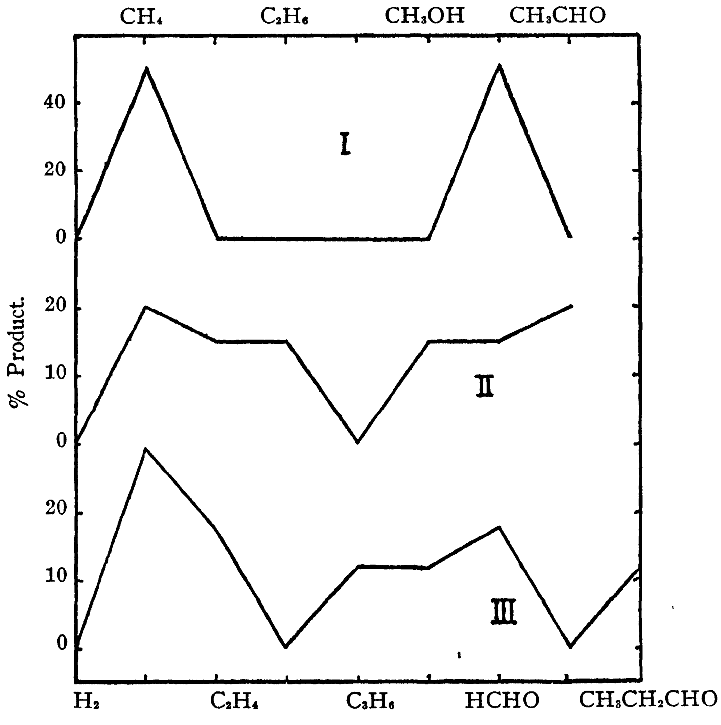


FIG. 25.—Calculated products in the thermal decomposition of dimethyl ether (I), methyl ethyl ether (II), and methyl propyl ether (III).

Dimethyl Ether.—CH_3OCH_3. The decomposition of dimethyl ether may be represented by:

$$\begin{aligned}
&P_1\quad CH_3OCH_3 \rightarrow CH_3 + CH_3O\\
&S_1\quad CH_3O \rightarrow HCHO + H
\end{aligned}$$

or

$$\begin{aligned}
&S_2\quad CH_3OCH_3 + CH_3O \rightarrow CH_3OH + CH_3OCH_2\\
&A_1\quad CH_3OCH_3 + R \rightarrow RH + CH_3OCH_2\\
&\qquad\qquad\qquad\qquad \rightarrow RH + HCHO + CH_3\\
&\qquad\qquad\qquad R = CH_3.
\end{aligned}$$

The decomposition of dimethyl ether should therefore produce equimolecular amounts of methane and formaldehyde.

Methyl Ethyl Ether.—$CH_3OCH_2CH_3$. This decomposition can be represented by three chain cycles as follows:[1]

$$\begin{aligned}
&A_1\quad C_3H_8O + R \rightarrow RH + CH_2OCH_2CH_3\\
&\qquad\qquad\qquad \rightarrow RH + HCHO + CH_3CH_2\\
&A_2\quad C_3H_8O + R \rightarrow RH + CH_3OCH_2CH_2\\
&\qquad\qquad\qquad \rightarrow RH + C_2H_4 + CH_3O\\
&A_3\quad C_3H_8O + R \rightarrow RH + CH_3OCHCH_3\\
&\qquad\qquad\qquad \rightarrow RH + CH_3CHO + CH_3\\
&\qquad\qquad R = CH_3, CH_3CH_2, CH_3O.
\end{aligned}$$

The decomposition may be summarized:

$$\begin{aligned}
&A_1\quad 3\,C_3H_8O \rightarrow 3\,HCHO + 3\,C_2H_6\\
&A_2\quad 3\,C_3H_8O \rightarrow 3\,C_2H_4 + 3\,CH_3OH\\
&A_3\quad 4\,C_3H_8O \rightarrow 4\,CH_3CHO + 4\,CH_4
\end{aligned}$$

Diethyl ether.—$CH_3CH_2O\,CH_2CH_3$. The decomposition may be represented:

$$\begin{aligned}
&A_1\quad C_4H_{10}O + R \rightarrow RH + CH_2CH_2OCH_2CH_3\\
&\qquad\qquad\qquad \rightarrow RH + C_2H_4 + CH_3CH_2O\\
&\qquad\qquad\qquad \rightarrow RH + C_2H_4 + HCHO + CH_3\\
&A_2\quad C_4H_{10}O + R \rightarrow RH + CH_3CHOCH_2CH_3\\
&\qquad\qquad\qquad \rightarrow RH + CH_3CHO + CH_3CH_2
\end{aligned}$$

---

[1] We have assumed that the methoxy radical does not decompose; however it may be that it is unstable and decomposes to formaldehyde and a hydrogen atom.

These chains may then be summarized:

$$A_1 \quad 6\,C_4H_{10}O \rightarrow 6\,C_2H_4 + 6\,HCHO + 6\,CH_4$$

$$A_2 \quad 8\,C_4H_{10}O \rightarrow 8\,CH_3CHO + 8\,C_2H_6$$

All ethers which have the general formula RCH_2OCH_2R' would be expected to decompose in an exactly similar manner to produce paraffin hydrocarbons and aldehyes; carbon monoxide should not occur as a primary product.

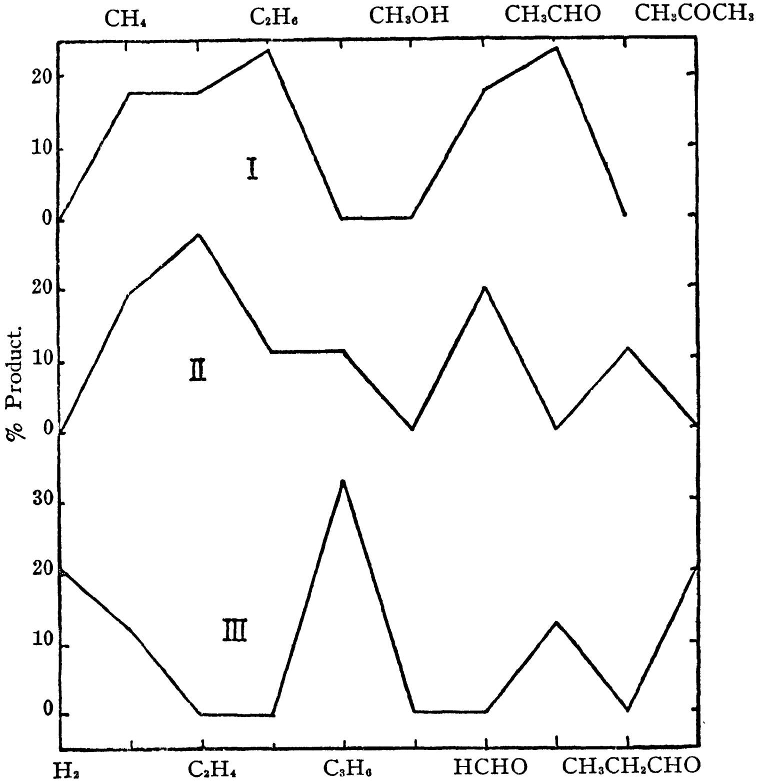
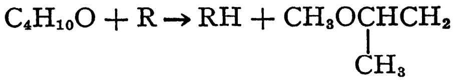


FIG. 26.—Calculated products in the thermal decomposition of diethyl ether (I), dipropyl ether (II) and di-isopropyl ether (III).

Methyl Isopropyl Ether.—$CH_3OCH(CH_3)_2$. The chain reactions may be represented as follows:

A₁ 

$$C_4H_{10}O + R \rightarrow RH + CH_3O\underset{CH_3}{\underset{|}{C}}HCH_2$$

$$\rightarrow RH + C_3H_6 + CH_3O$$

$$\begin{aligned} A_2 \quad C_4H_{10}O + R &\rightarrow RH + CH_2O\,CH(CH_3)_2 \\ &\rightarrow RH + HCHO + CH_3CHCH_3 \\ &\rightarrow RH + HCHO + C_3H_6 + H \end{aligned}$$

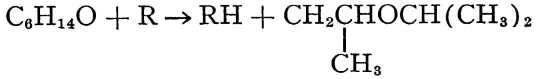
$$\begin{aligned} A_3 \quad C_4H_{10}O + R &\rightarrow RH + CH_3OC(CH_3)_2 \\ &\rightarrow RH + CH_3COCH_3 + CH_3 \end{aligned}$$

$$R = H, CH_3, CH_3O.$$

The decomposition may be summarized:

$$\begin{aligned} A_1 \quad 6\,C_4H_{10}O &\rightarrow 6\,C_3H_6 + 6\,CH_3OH \\ A_2 \quad 3\,C_4H_{10}O &\rightarrow 3\,HCHO + 3\,C_3H_6 + 3\,H_2 \\ A_3 \quad 10\,C_4H_{10}O &\rightarrow 10\,CH_3COCH_3 + 10\,CH_4 \end{aligned}$$

Di-isopropyl ether.—$(CH_3)_2CHOCH(CH_3)_2$. The decomposition may be represented as follows:

A₁ 

$$C_6H_{14}O + R \rightarrow RH + CH_2\underset{CH_3}{\underset{|}{C}}HOCH(CH_3)_2$$

$$\begin{aligned} &\rightarrow RH + C_3H_6 + (CH_3)_2CHO \\ &\rightarrow RH + C_3H_6 + CH_3CHO + CH_3 \end{aligned}$$

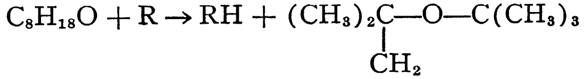
$$\begin{aligned} A_2 \quad C_6H_{14}O + R &\rightarrow RH + (CH_3)_2COCH(CH_3)_2 \\ &\rightarrow RH + CH_3COCH_3 + CH_3CHCH_3 \\ &\rightarrow RH + CH_3COCH_3 + C_3H_6 + H \end{aligned}$$

$$R = H, CH_3.$$

These chains may be summarized:

$$\begin{aligned} A_1 \quad 12\,C_6H_{14}O &\rightarrow 12\,C_3H_6 + 12\,CH_3CHO + 12\,CH_4 \\ A_2 \quad 20\,C_6H_{14}O &\rightarrow 20\,CH_3COCH_3 + 20\,C_3H_6 + 20\,H_2 \end{aligned}$$

Di-tert.-butyl ether.—$(CH_3)_3C—O—C(CH_3)_3$. There is only one chain reaction:

A₁ 

$$C_8H_{18}O + R \rightarrow RH + (CH_3)_2\underset{CH_2}{\underset{|}{C}}—O—C(CH_3)_3$$

$$\begin{aligned} &\rightarrow RH + C_4H_8(iso) + (CH_3)_3C—O^{\cdot} \\ &\rightarrow RH + C_4H_8(iso) + CH_3COCH_3 + CH_3 \end{aligned}$$

$$R = CH_3.$$

This may be summarized:

$$A_1 \quad C_8H_{18}O \rightarrow CH_4 + C_4H_8(\text{iso}) + CH_3COCH_3.$$

All ethers containing a secondary or tertiary carbon atom attached to the oxygen atom should decompose through a chain cycle which produces a ketone as one of the products.

The calculated decomposition products of a number of ethers are shown graphically in Figs. 25 and 26; experimental data do not appear to be available at present. However, an attempt has been made to obtain comparison with experimental results by calculating the decomposition products for complete decomposition of the formaldehyde and acetaldehyde formed and comparing these results with data from gas analyses made by Hinshelwood[2] and his co-workers. The results are in good agreement for dimethyl ether but the agreement is not so good

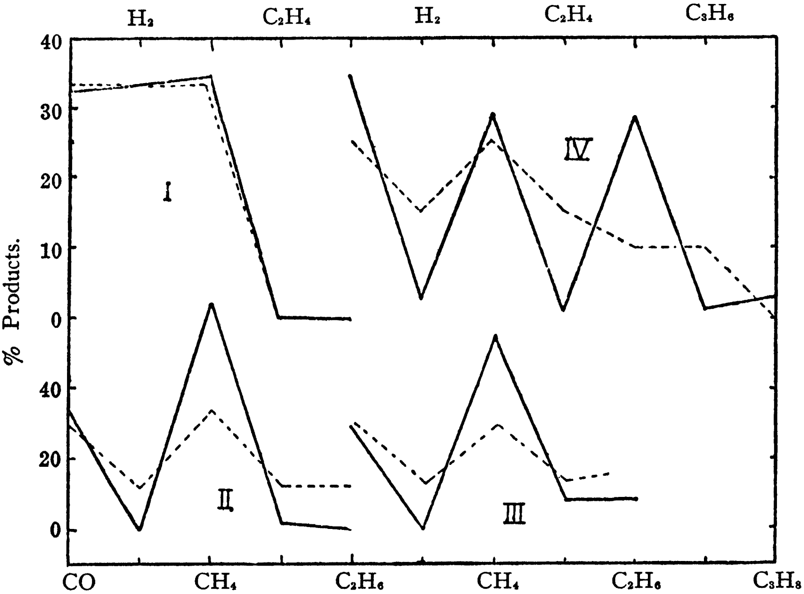


FIG. 27.—Gases formed in the decomposition of ethers assuming complete decomposition of aldehydes. I dimethyl ether; II methyl ethyl ether; III diethyl ether; IV methyl propyl ether. Calculated - - - - ; experimental ——.

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[2] Hinshelwood and Askey, *Proc. Roy. Soc.*, **A 115**, 215 (1927); Hinshelwood, *ibid.*, **114**, 84 (1927); Glass and Hinshelwood, *J. Chem. Soc.*, **1084**, 1815 (1929).

for diethyl ether, methyl ethyl ether and methyl propyl ether. The calculated and experimental curves are shown in Fig. 27. A further comparison between theory and experiment may be made by comparing the calculated and observed increase in pressure for complete decomposition; this has been done in Table V.

TABLE V

NUMBER OF MOLS OF PRODUCTS FROM 1 MOL OF ETHER, ASSUMING COMPLETE DECOMPOSITION OF HCHO AND CH_3CHO

Ether	Calculated	Observed
Dimethyl	3	3
Methyl Ethyl	2.7	2.7
Diethyl	3.4	2.9
Methyl Propyl	2.9	2.6
Di-isopropyl	3.4	3.3

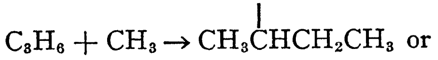
CHAPTER X

OLEFINIC HYDROCARBONS

The decomposition of the unsaturated hydrocarbons presents several problems which do not arise in connection with other classes of compounds. In the first place, the double bond profoundly influences the chemical reactivity of the hydrogen atoms adjacent to it; thus, the α hydrogen atoms, i. e. those attached directly to a doubly bound carbon atom, are extremely inactive; whereas the β hydrogen atoms, on the other hand, are extremely reactive. This must mean that the C—H bonds in the α position are very strong, and that those in the β position are correspondingly weak. We have assumed that the strength of a β C—H bond in an olefin is at least 6 Cal. less than that of a primary C—H bond in a paraffin hydrocarbon, and that, on the other hand, the strength of the bond holding the α hydrogen atom is increased by approximately the same amount. It follows from these assumptions that in any reaction between a free radical R and an olefinic molecule the β hydrogen atoms will be attacked almost exclusively, unless of course association takes place, in which case the radical will add to one of the carbon atoms of the double bond. We have further assumed that the activation energy of the reaction R + olefinic hydrocarbon to give RH + R′ (where R represents an alkyl radical larger than ethyl) is sufficiently small that it occurs in preference to the decomposition of R into an olefin and a smaller radical; this assumption applies of course only at pressures not too far below atmospheric since at low pressure the unimolecular decomposition of the radical R would be expected to occur.

In the second place, there is the further difficulty that a free radical can add to an unsaturated hydrocarbon, usually in either of two ways, as well as abstract a β hydrogen atom from the molecule. We may consider the reaction between propylene and a free methyl group as an example:

(1) $$C_3H_6 + CH_3 \rightarrow CH_4 + {-}CH_2CH{=}CH_2 \text{ or}$$

(2) 

$$C_3H_6 + CH_3 \rightarrow CH_3\overset{|}{C}HCH_2CH_3 \text{ or}$$

(3) $$C_3H_6 + CH_3 \rightarrow (CH_3)_2CHCH_2{-}$$

Reactions (2) and (3) are association reactions of the type studied by Taylor and Jones.[1] It seems probable that this type of reaction predominates in the lower ranges of temperature; if free radicals are produced at a sufficiently low temperature this type of reaction may even occur exclusively.

We shall consider the decomposition of olefinic hydrocarbons only under such conditions of temperature that the addition reactions of the radicals to the hydrocarbon can be neglected. There is considerable experimental evidence that the course of the decomposition of olefinic hydrocarbons is the same over the entire range 600–950° C. For example, Hurd and Meinert[2] studied the decomposition of propylene from 600–700° C. as well as at 950° C. They conclude, " Comparison of these runs with the others shows that pyrolysis at 950° C. in quartz with a hot contact time of one-half second gives about the same results as pyrolysis at 700° in Pyrex with a contact time of fifty-three seconds. The percentage of propylene pyrolyzed is about 90 instead of 73, but the products formed are very much the same. There is about the same percentage of unrecovered propylene which is converted into liquids in each case, viz., 20–25%. In both cases liquids are aromatic hydrocarbons and in both the gaseous products are the same."

The peculiar character of the radicals formed is such that the course of the decomposition of the lower members of the olefin series is quite different from that of most other classes of organic compounds. If we consider again, for example, the reaction

$$CH_3 + CH_3CH{=}CH_2 \rightarrow CH_4 + {-}CH_2CH{=}CH_2,$$

we find that the methyl group combines with one of the three β hydrogen atoms of propylene to form methane and the free allyl radical. Following the reasoning used in the previous chapters the decomposition of the allyl radical might be expected to be:

$$-CH_2CH{=}CH_2 \rightarrow CH_2{=}C{=}CH_2 + H.$$

In this way, a chain reaction, with allene and hydrogen as the chief products, would be initiated. But quite apart from the fact that allene has not been detected among the products of the thermal decomposition of propylene and its homologues, there does not seem to be any justification for writing the allyl radical as $-CH_2CH{=}CH_2$; actually all three carbon atoms are unsaturated and it is probably more correct to write the formula $\overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2}$, with the line over each carbon atom representing a free valency. Because of a resonance effect[3] a structure of this kind may be much more stable than an ordinary free radical. There are three types of reactions that such an allyl radical can undergo when surrounded by propylene molecules: first, one of the end carbon atoms of the radical can react with a β hydrogen atom of one of the propylene molecules, simply regenerating propylene and forming a new allyl radical. Second, the middle carbon atom of the radical can take a hydrogen atom from a propylene molecule and then either isomerise according to the equations,

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[1] Taylor and Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

[2] Hurd and Meinert, *J. Am. Chem. Soc.*, **52**, 4987 (1932).

$$\overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2} + \mathrm{CH_3CH{=}CH_2} \rightarrow \overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2} + \mathrm{{-}CH_2CH_2CH_2{-}}$$

$$\mathrm{{-}CH_2CH_2CH_2{-}} \rightarrow \mathrm{CH_3CH{=}CH_2}$$

or initiate a building up process to propane;[4] but in this case also the allyl radical is regenerated: every allyl radical that changes to propane is replaced by three other allyl radicals, as illustrated by the following equations:

$$\mathrm{C_3H_6} + \overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2} \rightarrow \overset{|}{\mathrm{C}}\mathrm{H_2}\mathrm{CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2} + \overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2}$$

$$\mathrm{C_3H_6} + \overset{|}{\mathrm{C}}\mathrm{H_2}\mathrm{CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2} \rightarrow \mathrm{CH_3CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2} + \overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2}$$

$$\mathrm{C_3H_6} + \mathrm{CH_3CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2} \rightarrow \mathrm{C_3H_8} + \overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2}$$

Third, since we have assumed that the allyl radical does not decompose under these conditions and since all the reactions with the surrounding molecules regenerate it, it can finally disappear only through collision with itself to produce diallyl. Naturally this mechanism applies only to the very early stages of the reaction; as the concentration of the diallyl rises it will decompose[5] presumably yielding the oily products obtained in the experimental decomposition of propylene.

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[3] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); *idem.*, *J. Am. Chem. Soc.*, **54**, 988 (1932); Yabroff, Branch, and Bettman, *ibid.*, **56**, 1850 (1934).

[4] This building up process can occur only if the isomerisation of the radical $\mathrm{{-}CH_2CH_2CH_2{-}}$ requires an appreciable activation energy. High pressure would favor the building up process.

[5] See Hurd, *Ind. Eng. Chem.*, **26**, 50 (1934).

The special structure of these unsaturated radicals leads to one other effect not brought about by other radicals. On this basis it is possible to account for the isomerisation of the olefinic hydrocarbons during their thermal decomposition, as well as for the hydrogenation and diolefine formation that have already been discussed. We may illustrate the possibility of isomerisation with reference to the two radicals

$$\begin{array}{ccc} \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 & \text{and} & \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}HCH_3. \\ 1\quad 2\quad 3 & & 1\quad 2\quad 3\quad 4 \end{array}$$

In the case of the first radical, carbon atoms number 1 and 3 are interchangeable: when either of them adds a hydrogen from one of the surrounding molecules propylene is formed. On the other hand, when carbon atom number 1 of the second radical adds a hydrogen atom, butene–2 is formed, whereas when carbon atom number three reacts butene–1 is produced. With either radical, when the second carbon atom adds a hydrogen atom, isomerisation to an olefin hydrocarbon may occur or a building up process to the corresponding paraffin hydrocarbon may be initiated.

The first step in the decomposition of the lower members of the olefinic hydrocarbons is presumably a rupture of a C—C bond in the β position to the double bond. The radicals thus formed attack the surrounding molecules to form an allyl type of radical which can only disappear through collision with itself. There is no chain cycle, other than one of regeneration. On the other hand, the higher members of the olefin series decompose according to a chain mechanism, with the production of a paraffin hydrocarbon plus a molecule of the butadiene type of structure with a conjugated double bond. The detailed mechanism of both these types of reactions will be discussed and illustrated in the following pages.

Propylene.—$CH_3CH{=}CH_2$. The decomposition may be represented as follows:

$P_1 \quad C_3H_6 \rightarrow —CH_3 + CH_2{=}CH—$

$S_1 \quad C_3H_6 + —CH_3 \rightarrow CH_4 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2$

$S_2 \quad C_3H_6 + CH_2{=}CH— \rightarrow C_2H_4 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2.$

The chief gaseous products of the reaction should be, therefore, methane and ethylene in equal proportions. There is no chain reaction because the allyl group simply regenerates itself and forms propylene when either of the end carbon atoms takes a hydrogen atom from a propylene molecule; or, when the middle carbon atom adds a hydrogen atom it either isomerises to propylene or finally forms propane[4] according to the following equations:

$$S_3 \quad C_3H_6 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 \rightarrow \overset{|}{C}H_2CH_2\overset{|}{C}H_2 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2$$

$$S_4 \quad C_3H_6 + \overset{|}{C}H_2CH_2\overset{|}{C}H_2 \rightarrow CH_3CH_2\overset{|}{C}H_2 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2$$

$$S_5 \quad C_3H_6 + CH_3CH_2\overset{|}{C}H_2 \rightarrow C_3H_8 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2.$$

Each allyl radical that becomes propane is replaced, therefore, by three other allyl radicals obtained from three molecules of propylene. The allyl radicals that do not become propane must eventually combine with each other to form diallyl which as it accumulates in the system subsequently also decomposes to form the liquid products found. It is clear from the above equations that two out of every three molecules of propylene decomposed appear as diallyl (initially) and this fraction is independent of the amount of propane produced. At present it does not seem possible to make any very definite predictions regarding the extent of propane formation; probably at atmospheric pressure or lower it would be small or negligible. According to this mechanism therefore, the overall decomposition of propylene should be represented by the equation:

$$3\,C_3H_6 \rightarrow CH_4 + CH_2{=}CH_2 + CH_2{=}CHCH_2CH_2CH{=}CH_2.$$

Hurd and Meinert[6] have studied this decomposition in the range 600—900° in glass and silica vessels, and have found the reaction to be predominantly homogeneous and unimolecular. Table VI contains a summary of part of their results and represents the relative composition of the products expressed in moles.

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[6] Hurd and Meinert, *J. Am. Chem. Soc.*, **52**, 4978 (1930). The experimental results published are not in agreement; Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931), report that about half the propylene decomposed gives ethylene and the butenes. See also Hurd and Eilers, *ibid.*, **26**, 776 (1934).

TABLE VI

THERMAL DECOMPOSITION OF PROPYLENE

Relative Composition of Products expressed in Moles

% decomp.	15.5	16	26.7	29.7	38.4	50.8
Temp.	600°	650°	600°	600°	650°	700°
Paraffins	1.00	1.00	1.00	1.00	1.00	1.00
Ethylene	0.81	0.74	0.88	0.72	0.69	0.71
Hydrogen	0.20	0.20	0.31	0.18	0.23	0.27
Higher olefins	....	0.14	0.06	0.02	....	0.04
Acetylenes	....	0.08	0.13	0.04	....	0.02

The paraffin hydrocarbons consisted of approximately 75% methane and 25% higher hydrocarbons, principally ethane. From 20—25% of the propylene decomposed was converted into an oil in which benzene and toluene were identified.

Butene–1.—$CH_3CH_2CH{=}CH_2$. The decomposition may be represented as follows:

$$P_1 \quad C_4H_8\text{—}1 \rightarrow \text{—}CH_3 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2$$

$$S_1 \quad C_4H_8\text{—}1 + \text{—}CH_3 \rightarrow CH_4 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

$$S_2 \quad C_4H_8\text{—}1 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 \rightarrow C_3H_6 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

The main products of the reaction should therefore be methane and propylene. The former will predominate in the final products if some of the allyl radicals react to form propane according to the following equations:

$$S_3 \quad C_4H_8\text{—}1 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 \rightarrow \overset{|}{C}H_2CH_2\overset{|}{C}H_2 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

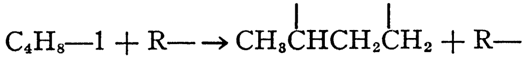
$$S_4 \quad C_4H_8\text{—}1 + \overset{|}{C}H_2CH_2\overset{|}{C}H_2 \rightarrow CH_3CH_2\overset{|}{C}H_2 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

$$S_5 \quad C_4H_8\text{—}1 + CH_3CH_2\overset{|}{C}H_2 \rightarrow C_3H_8 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

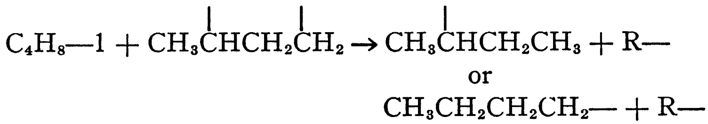
The radical $CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$ will react with the surrounding butene–1 molecules to regenerate itself and form either butene–1 or butene–2 or n–butane, according to the following equations, in which this radical is designated by the symbol R:

$S_6\quad C_4H_8{-}1 + R{-} \rightarrow C_4H_8{-}1 + R{-}$

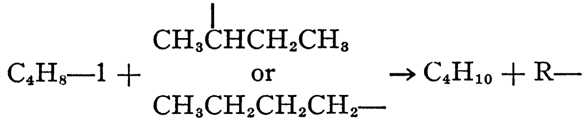
$S_7\quad C_4H_8{-}1 + R{-} \rightarrow C_4H_8{-}2 + R{-}$

S_8 

$$C_4H_8{-}1 + R{-} \rightarrow CH_3\overset{|}{C}HCH_2\overset{|}{C}H_2 + R{-}$$

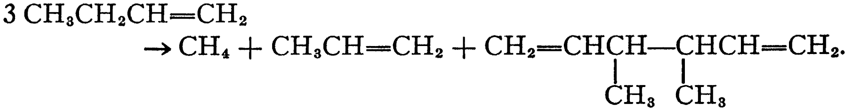
S_9 

$$C_4H_8{-}1 + CH_3\overset{|}{C}HCH_2\overset{|}{C}H_2 \rightarrow CH_3\overset{|}{C}HCH_2CH_3 + R{-} \text{ or } CH_3CH_2CH_2CH_2{-} + R{-}$$

S_{10} 

$$C_4H_8{-}1 + \begin{matrix} CH_3\overset{|}{C}HCH_2CH_3 \\ \text{or} \\ CH_3CH_2CH_2CH_2{-} \end{matrix} \rightarrow C_4H_{10} + R{-}$$

Possibly the radical $—CH_2CH_2CH_2—$ in equation S_3 isomerises very easily to propylene and similarly the radical $CH_3CHCH_2CH_2$ in equation S_8 isomerises very easily to butene–2. The overall decomposition of butene–1 should then be represented by the equation



$$3\,CH_3CH_2CH{=}CH_2 \rightarrow CH_4 + CH_3CH{=}CH_2 + CH_2{=}CH\underset{CH_3}{\underset{|}{C}}H{-}\underset{CH_3}{\underset{|}{C}}HCH{=}CH_2.$$

The decomposition should be accompanied by isomerisation to butene–2.

There are very few experimental results, for small percentage decomposition of the butene, available. Calingaert reports an experiment[7] in which butene–1 was cracked; the saturated gas contained hydrogen and methane and the unsaturated fraction contained propylene with a small amount of butadiene. More recently Hurd reports[5] the result of an experiment in which 57% of the butene–1 was decomposed; each 100 moles of butene–1 decomposed yielded 20 moles of butene–2, 44 moles of paraffin hydrocarbons (chiefly methane), 33 moles of propylene and 3.7 moles of hydrogen; 30% by weight of the butene–1 decomposed was recovered as liquids. Other results[5a] indicate that ethylene is a primary product of the decomposition; if this is so a second primary rupture according to the equation,

$$P_2\qquad C_4H_8{-}1 \rightarrow CH_3CH_2{-} + CH_2{=}CH{-},$$

would lead to the overall decomposition:

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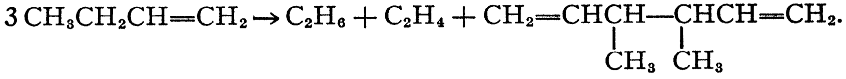
[7] Calingaert, *J. Am. Chem. Soc.*, **45**, 134 (1923).

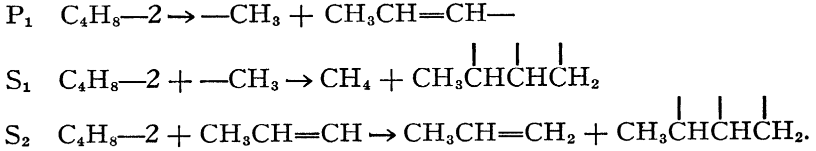
[5a] Hurd and Goldsby, *J. Am. Chem. Soc.*, **56**, 1812 (1934).



$$3\,CH_3CH_2CH{=}CH_2 \rightarrow C_2H_6 + C_2H_4 + CH_2{=}CH\underset{CH_3}{C}H{-}\underset{CH_3}{C}HCH{=}CH_2.$$

However since this involves rupture of the β C—C bond, the decomposition into methane and propylene which involves rupture of the weaker α C—C bond should predominate.

Butene–2.—$CH_3CH{=}CHCH_3$. The decomposition may be represented as follows:



P_1 $C_4H_8{-}2 \rightarrow {-}CH_3 + CH_3CH{=}CH{-}$

S_1 $C_4H_8{-}2 + {-}CH_3 \rightarrow CH_4 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$

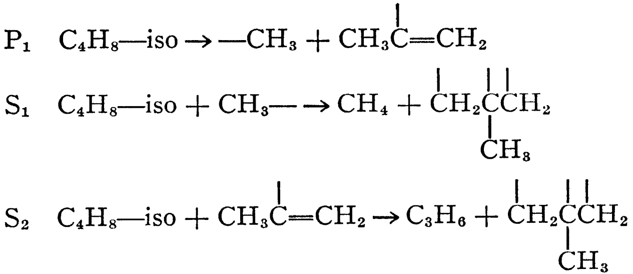
S_2 $C_4H_8{-}2 + CH_3CH{=}CH \rightarrow CH_3CH{=}CH_2 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2.$

The detailed mechanism is similar to that given for butene–1 and leads to the following overall equation for the decomposition:

$$3\,CH_3CH{=}CHCH_3 \rightarrow CH_4 + CH_3CH{=}CH_2 + CH_3CH{=}CHCH_2CH_2CH{=}CHCH_3.$$

This would be accompanied by isomerisation to butene–1. Actually, in the experimental decomposition of both butene–1 and butene–2 isomerisation probably plays a sufficiently important part that in any pyrolysis one is really studying the decomposition of a mixture of the two substances.

Iso-butylene.—$CH_3{-}\underset{CH_3}{C}{=}CH_2$. The decomposition of this compound may be represented as follows:

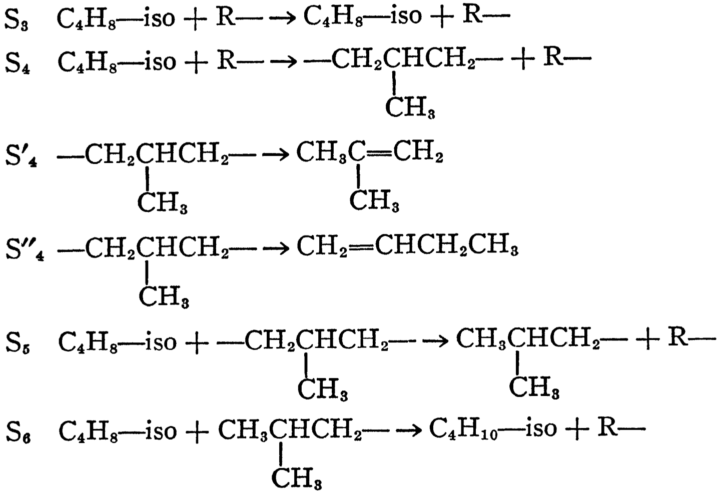


P_1 $C_4H_8{-}iso \rightarrow {-}CH_3 + CH_3\overset{|}{C}{=}CH_2$

S_1 $C_4H_8{-}iso + CH_3{-} \rightarrow CH_4 + \overset{|}{C}H_2\underset{CH_3}{\overset{|}{C}}\overset{|}{C}H_2$

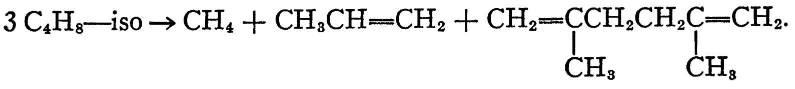
S_2 $C_4H_8{-}iso + CH_3\overset{|}{C}{=}CH_2 \rightarrow C_3H_6 + \overset{|}{C}H_2\underset{CH_3}{\overset{|}{C}}\overset{|}{C}H_2$

Although the radical $\overset{|}{C}H_2\underset{CH_3}{\overset{|}{C}}\overset{|}{C}H_2$ is symmetrical, there is the possibility of isomerisation to butene–1. This may occur if the middle carbon atom should capture a hydrogen atom from the surrounding isobutylene molecules; the radical $\text{—CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—}$ may either build up to isobutane or isomerise; the isomerisation may occur by migration of the middle hydrogen atom regenerating isobutylene or by migration of the methyl group forming butene–1. If one of the end carbon atoms captures a hydrogen atom from one of the surrounding isobutylene molecules another isobutylene molecule is regenerated. The following equations in which R is the radical $\overset{|}{\text{C}}\text{H}_2\overset{|}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}\overset{|}{\text{C}}\text{H}_2$ represent these reactions:



$$
\begin{aligned}
&S_3 \quad \text{C}_4\text{H}_8\text{—iso} + \text{R—} \rightarrow \text{C}_4\text{H}_8\text{—iso} + \text{R—}\\
&S_4 \quad \text{C}_4\text{H}_8\text{—iso} + \text{R—} \rightarrow \text{—CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} + \text{R—}\\
&S'_4 \quad \text{—CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} \rightarrow \text{CH}_3\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{=CH}_2\\
&S''_4 \quad \text{—CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} \rightarrow \text{CH}_2\text{=CHCH}_2\text{CH}_3\\
&S_5 \quad \text{C}_4\text{H}_8\text{—iso} + \text{—CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} \rightarrow \text{CH}_3\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} + \text{R—}\\
&S_6 \quad \text{C}_4\text{H}_8\text{—iso} + \text{CH}_3\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{HCH}_2\text{—} \rightarrow \text{C}_4\text{H}_{10}\text{—iso} + \text{R—}
\end{aligned}
$$

According to this mechanism, the overall decomposition should be represented by the equation:



$$3\,\text{C}_4\text{H}_8\text{—iso} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH=CH}_2 + \text{CH}_2\text{=}\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{CH}_2\text{CH}_2\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{=CH}_2.$$

This may be expected to be accompanied by some isomerisation to butene–1 according to equation S''_4 and by some hydrogenation to isobutane according to equations S_5 and S_6.

The decomposition of isobutylene has been carefully studied by Hurd and Spence;[8] we have summarized a part of their results as follows:

Temp.	652°	599°	652°	700°
% Decomposed	11.1	20	22.7	30.2
CH_4	1.00	1.00	1.00	1.00
Propylene	1.07	0.51	0.60	0.35
Isobutane	1.47	0.46	0.62	0.20
Hydrogen	0.4	0.30	0.52	0.37
Acetylene	0.8	0.03	0.12	0.06

The methane-propylene ratio for the 11.1% decomposition and the presence of isobutane are in accord with our mechanism. About 60% of the isobutylene decomposed was recovered in the form of an oil.

Pentene–1.—$CH_3CH_2CH_2CH{=}CH_2$. The decomposition of this compound may be represented as follows:

$$P_1 \quad C_5H_{10}\text{—}1 \rightarrow CH_3CH_2\text{—} + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2$$

$$S_1 \quad C_5H_{10}\text{—}1 + CH_3CH_2\text{—} \rightarrow C_2H_6 + CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

$$S_2 \quad C_5H_{10}\text{—}1 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 \rightarrow C_3H_6 + CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

These reactions are not of any special importance in this case in connection with the products formed, because a chain reaction takes place in this decomposition.

$$\begin{aligned} A_1 \quad C_5H_{10}\text{—}1 + R &\rightarrow RH + CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2 \\ &\rightarrow RH + CH_2{=}CHCH{=}CH_2 + CH_3\text{—} \\ R &= CH_3\text{—}. \end{aligned}$$

This chain leads to the production of methane and butadiene in equal proportions and these should therefore be the main products of the decomposition.

It is possible that an interchange reaction occurs between the chain radical $CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$ and the pentane–1, either regenerating pentene–1 or forming pentene–2 if the end carbon atom of the chain radical takes a hydrogen atom from the surrounding molecules. Hurd[8a] has reported the presence of isopropyl ethylene but it does not seem possible to account for this substance as a primary product. Possibly it comes from a reaction between a methyl radical and butadiene to form the radical $-CH_2-\underset{CH_3}{\underset{|}{C}}H-CH{=}CH_2$ which could remove a hydrogen from pentene–1 to form isopropyl ethylene. Addition of butadiene at the beginning of the decomposition should increase the yield of isopropyl ethylene if it is formed in this way.

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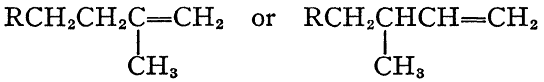
[8] Hurd and Spence, *J. Am. Chem. Soc.*, **51**, 3561 (1929).

[8a] Hurd, *Ind. Eng. Chem.*, **26**, 50 (1934).

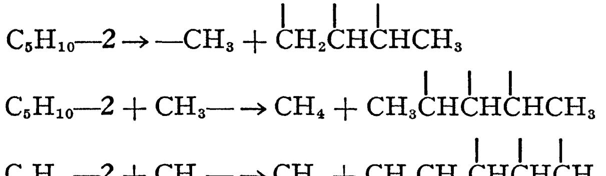
It can easily be shown that all hydrocarbons of the general formula $RCH_2CH_2CH{=}CH_2$ will decompose in the same way by a chain mechanism, to yield as the main products butadiene and a saturated hydrocarbon RH; further, all compounds of the formula



$$RCH_2CH_2\underset{CH_3}{\underset{|}{C}}{=}CH_2 \quad \text{or} \quad RCH_2\underset{CH_3}{\underset{|}{C}}HCH{=}CH_2$$

should decompose in the same way to yield as the main products isoprene, $CH_2{=}\underset{CH_3}{\underset{|}{C}}-CH{=}CH_2$ and a saturated hydrocarbon.

Pentene–2.—$CH_3CH_2CH{=}CHCH_3$. This decomposition may be represented as follows:

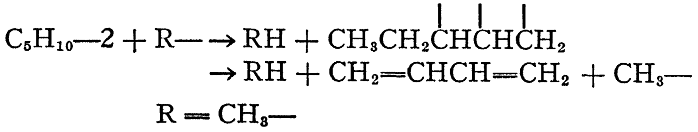


$$P_1 \quad C_5H_{10}-2 \rightarrow -CH_3 + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}HCH_3$$

$$S_1 \quad C_5H_{10}-2 + CH_3- \rightarrow CH_4 + CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}HCH_3$$

$$S_2 \quad C_5H_{10}-2 + CH_3- \rightarrow CH_4 + CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

We have the two alternative reactions, S_1 and S_2, because pentene–2 contains two kinds of β hydrogen atoms. There seems some possibility that the entire decomposition may go through a chain process involving the radical $CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$; it is also possible that the radical $CH_3\overset{|}{C}H\overset{|}{C}H\overset{|}{C}HCH_3$ may show some stability due to a resonance effect and either build up to pentane or change to the radical $CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$ by taking hydrogen atoms from the surrounding molecules of pentene–2. In the latter case the chain mechanism would be:



$$A_1 \quad C_5H_{10}-2 + R- \rightarrow RH + CH_3CH_2\overset{|}{C}H\overset{|}{C}H\overset{|}{C}H_2$$

$$\rightarrow RH + CH_2{=}CHCH{=}CH_2 + CH_3-$$

$$R = CH_3-$$

and the main products of the decomposition would be methane and butadiene, as in the case of pentene–1. These olefin reactions should however be very sensitive to pressure; pressures approaching atmospheric or higher and low temperature of decomposition would be expected to favor isomerisation, whereas lower pressures and higher temperatures would favor the chain mechanisms.

Norris and Reuter[9] have analyzed the products formed when pentene–2 is decomposed in a carbon coated silica tube, but they have studied only higher percentage decompositions; part of their results are summarized as follows:

	CH_4 :	butadiene, 1, 3 :	butene :	propylene :	C_2H_4
1/3 decomp. 575° C..	1	0.3	10	2	0.5
2/3 decomp. 600° C..	1	0.3	0.27	0.21	0.15

About one-third of the products consisted of substances of higher molcular weight than pentene–2.

A summary of the products to be expected on the basis of the free radical theory for these olefins is given in Table VII. It is based on the assumption that the decomposition is conducted at fairly high temperatures (600° or higher) and pressures (approximately atmospheric or higher); there is of course the further condition that only a small fraction of the compound is decomposed.

TABLE VII

THERMAL DECOMPOSITION OF MONO-OLEFINS

Summary of Products formed

	Main Products	Subsidiary Products	Stable Radical	Liquids (Di-olefins)
Propylene	Methane Ethylene	Propane	$\overset{\vert}{C}H_2\overset{\vert}{C}H\overset{\vert}{C}H_2$	66%
Butene–1	Methane Propylene	Butene–2 Propane n-Butane	$CH_3\overset{\vert}{C}H\overset{\vert}{C}H\overset{\vert}{C}H_2$	66%
Butene–2	Methane Propylene	Butene–1 Propane n-Butane	$CH_3\overset{\vert}{C}H\overset{\vert}{C}H\overset{\vert}{C}H_2$	66%

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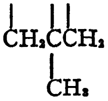
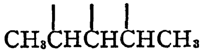
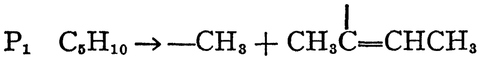
[9] Norris and Reuter, *J. Am. Chem. Soc.*, **49**, 2626 (1927); see also Hurd and Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934).

	Product Main	Subsidiary Products	Stable Radical	Liquids (Di-olefins)
Isobutylene	Methane Propylene	Isobutane	 $\overset{\vert}{C}H_2\underset{\underset{CH_3}{\vert}}{\overset{\vert\vert}{C}}H_3$	66%
Pentene–1	Methane Butadiene–1, 3	n-Pentane Pentene–2 Propane, ethane Propylene	None	Very small
Pentene–2	Methane Butadiene–1, 3	Pentene–1 n-Pentane Butene–1 and 2 n-Butane	 $CH_3\overset{\vert}{C}H\overset{\vert}{C}H\overset{\vert}{C}HCH_3$	Small

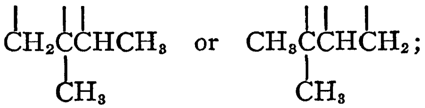
Trimethyl ethylene.—$(CH_3)_2C{=}CHCH_3$. The decomposition may be represented as follows:



$$P_1 \quad C_5H_{10} \rightarrow —CH_3 + CH_3\overset{|}{C}{=}CHCH_3$$

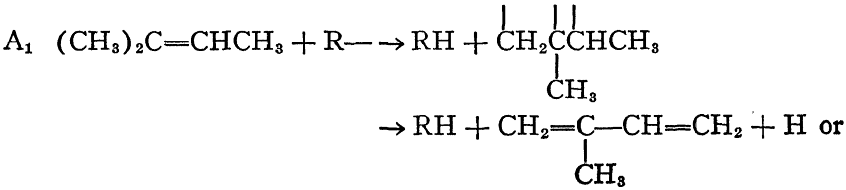
$$P_2 \quad C_5H_{10} \rightarrow —CH_3 + (CH_3)_2C{=}CH—$$

Removal of a β hydrogen atom from trimethyl ethylene must give either



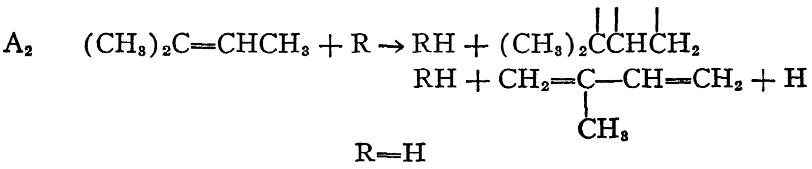
$$\overset{|}{C}H_2\underset{\underset{CH_3}{|}}{\overset{||}{C}}CHCH_3 \quad \text{or} \quad CH_3\underset{\underset{CH_3}{|}}{\overset{||}{C}}CH\overset{|}{C}H_2;$$

if these radicals can decompose by loss of a hydrogen atom to form isoprene the following chain cycles will take place:



$$A_1 \quad (CH_3)_2C{=}CHCH_3 + R— \rightarrow RH + \overset{|}{C}H_2\underset{\underset{CH_3}{|}}{\overset{||}{C}}CHCH_3$$

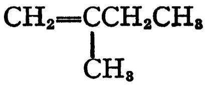
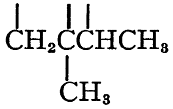
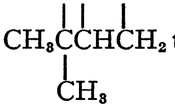
$$\rightarrow RH + CH_2{=}\underset{\underset{CH_3}{|}}{C}—CH{=}CH_2 + H \text{ or}$$



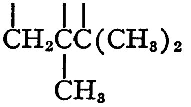
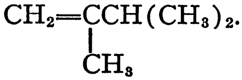
$$A_2 \quad (CH_3)_2C{=}CHCH_3 + R \rightarrow RH + (CH_3)_2\overset{||}{C}CH\overset{|}{C}H_2$$

$$RH + CH_2{=}\underset{\underset{CH_3}{|}}{C}—CH{=}CH_2 + H$$

$$R{=}H$$

Thus both cycles yield isoprene and hydrogen and these two substances should be the main products of the decomposition. Possibly these reactions may occur at low pressures and high temperatures. However if the two radicals can react with the trimethyl ethylene, there may be simply either a regeneration process or formation of  $CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2CH_3$ or $CH_3CH_2CH{=}CHCH_3$[10] depending upon which carbon atom of the radicals  $\overset{|}{C}H_2\underset{CH_3}{\underset{|}{\overset{|}{C}}}\overset{|}{C}HCH_3$ or  $CH_3\underset{CH_3}{\underset{|}{\overset{|}{C}}}\overset{|}{C}H\overset{|}{C}H_2$ takes a hydrogen atom from the surrounding trimethyl ethylene molecules.

Norris and Reuter[9] found that when trimethyl ethylene is 75% decomposed at 650° C. methane is the only saturated hydrocarbon produced and both hydrogen and butadiene are absent.

The same reasoning applies also to tetramethyl ethylene. If the radical  $\overset{|}{C}H_2\underset{CH_3}{\underset{|}{\overset{|}{C}}}\overset{|}{C}(CH_3)_2$ decomposes into 2, 3 dimethyl butadiene and a hydrogen atom a chain cycle is possible; on the other hand if it reacts with tetramethyl ethylene it may either regenerate itself or isomerise into $CH_3CH_2CH{=}C(CH_3)_2$ or  $CH_2{=}\underset{CH_3}{\underset{|}{C}}CH(CH_3)_2$.

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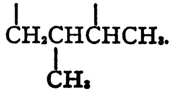
[10] This would be formed by rearrangement of the radical  $\overset{|}{C}H_2CH\underset{CH_3}{\underset{|}{\overset{|}{C}}}HCH_3$.

CHAPTER XI

OTHER ORGANIC COMPOUNDS

It seems to be desirable to give a brief treatment of the thermal decomposition of some other classes of compounds from the free radical standpoint, although only few reliable experimental data are available.[1] With the lower alcohols and acids, surface effects probably play an appreciable rôle although the extent does not appear to be known.

Alcohols.—From the fact that the lower aliphatic alcohols do not remove metallic mirrors very readily[2] it seems probable that the decomposition consists chiefly of the direct separation of molecular hydrogen and formation of the corresponding aldehyde or ketone. This may be represented as follows:

$$CH_3OH \rightarrow H_2 + HCHO$$

$$CH_3CH_2OH \rightarrow H_2 + CH_3CHO$$

$$CH_3CHOHCH_3 \rightarrow H_2 + CH_3COCH_3$$

These reactions are endothermic to the extent of approximately 30 Cal.; however they probably represent the only possible method for the direct separation of molecular hydrogen.

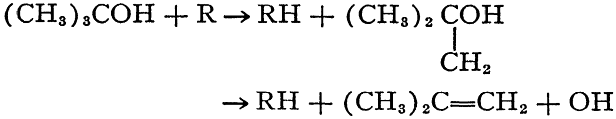
The decomposition of a higher alcohol, RCH_2CH_2OH, through the following chain,

$$\begin{aligned} RCH_2CH_2OH + R' &\rightarrow R'H + RCHCH_2OH \\ &\rightarrow R'H + RCH{=}CH_2 + OH \end{aligned}$$

$$R' = OH$$

would result in the formation of the corresponding olefin and water. However several other chains are possible, depending on the molecular weight and structure of the alcohol so that on the basis of a chain mechanism the products would be expected to be very complex.

The decomposition of tert. butyl alcohol should be an example of a particularly simple chain reaction:



$$\begin{aligned} (CH_3)_3COH + R &\rightarrow RH + (CH_3)_2\underset{\underset{\displaystyle CH_2}{|}}{C}OH \\ &\rightarrow RH + (CH_3)_2C{=}CH_2 + OH \end{aligned}$$

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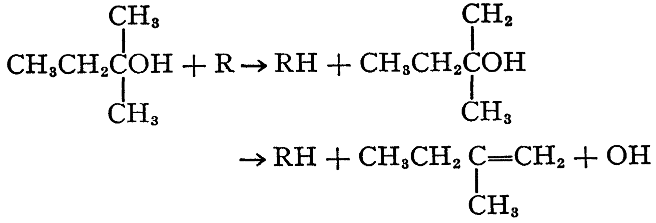
[1] See Hurd, *Pyrolysis of Carbon Compounds*, Chemical Catalog Co., 1929.

[2] Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3529 (1932) and unpublished work.

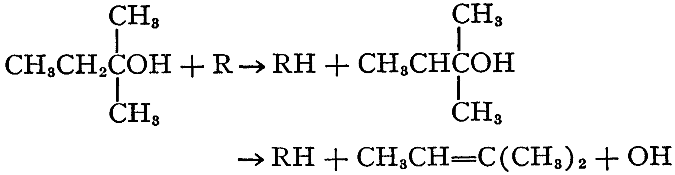
The products should be water and isobutylene. On the other hand, the decomposition of tert. amyl alcohol should occur through three chain reactions:

A_1



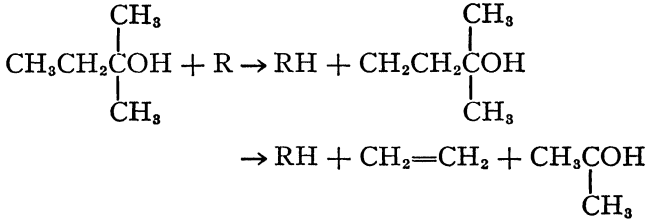
$$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}OH + R \rightarrow RH + CH_3CH_2\overset{CH_2}{\underset{CH_3}{C}}OH \rightarrow RH + CH_3CH_2\,\underset{CH_3}{C}{=}CH_2 + OH$$

A_2



$$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}OH + R \rightarrow RH + CH_3CH\overset{CH_3}{\underset{CH_3}{C}}OH \rightarrow RH + CH_3CH{=}C(CH_3)_2 + OH$$

A_3



$$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}OH + R \rightarrow RH + CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}OH \rightarrow RH + CH_2{=}CH_2 + CH_3\underset{CH_3}{C}OH$$

$R = OH, (CH_3)_2COH.$

At high pressures the chain reaction A_3 should produce ethylene and isopropyl alcohol, whereas at low pressures it should produce ethylene, acetone and hydrogen. Schultz and Kistiakowsky[2a] have investigated the kinetics of the thermal decomposition of tertiary butyl and tertiary amyl alcohols; the reactions are homogeneous and follow a unimolecular law and the measured activation energies are 65.5 and 60.0 Cal. respectively.

Acids.—Hurd[3] has shown that the formation of acetic anhydride in the thermal decomposition of acetic acid very probably results through the primary formation of ketene and its subsequent reaction with undecomposed acid. This evidence is in good agreement with the free radical mechanism:

[2a] Schultz and Kistiakowsky, *This Journal,* **56**, 395 (1934).

[3] Hurd, *Pyrolysis of Carbon Compounds,* p. 334. Chemical Catalog. Co., 1929.

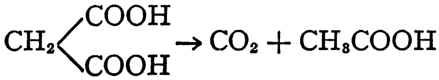
$$\begin{aligned} CH_3COOH + R &\rightarrow RH + CH_2COOH \\ &\rightarrow RH + CH_2{=}CO + OH. \end{aligned}$$

A similar chain for the higher acids presents two possibilities:

$$\begin{aligned} RCH_2CH_2COOH + R' &\rightarrow R'H + RCH_2CHCOOH \\ &\rightarrow R'H + CH_2{=}CHCOOH + R \\ \text{or } &\rightarrow R'H + RCH_2CH{=}CO + OH \end{aligned}$$

The first chain results in the formation of acrylic acid and a hydrocarbon, whereas in the second case the corresponding ketene is formed and hence the acid anhydride should be the final product.

When malonic acid or its homologues are heated there is loss of carbon dioxide and formation of a monobasic acid. The decomposition in the case of malonic acid is represented by the equation:



$$CH_2\begin{cases} COOH \\ COOH \end{cases} \rightarrow CO_2 + CH_3COOH$$

This decomposition has been studied experimentally by Hinshelwood,[4] and it was found that the pure liquid decomposes according to a unimolecular law with an activation energy of about 31 Cal. It does not seem possible to write any chain reaction which would explain this decomposition if we assume that the methylene hydrogen atoms are less strongly bound than the carboxyl hydrogen atoms. There is the possibility of the migration of one of the carboxyl hydrogen atoms to the central carbon atom with splitting off of carbon dioxide. If the decomposition of malonic acid were strongly exothermic and the corresponding decomposition of acetic acid

$$CH_3COOH \rightarrow CO_2 + CH_4,$$

were not, one might expect migration to occur in the decomposition of the former and not of the latter compound. Accordingly we calculated the heats of formation[5] of a number of acids and their product

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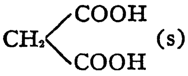
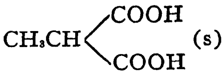
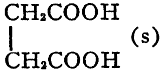
[4] Hinshelwood, *J. Chem. Soc.*, **117**, 156 (1920).

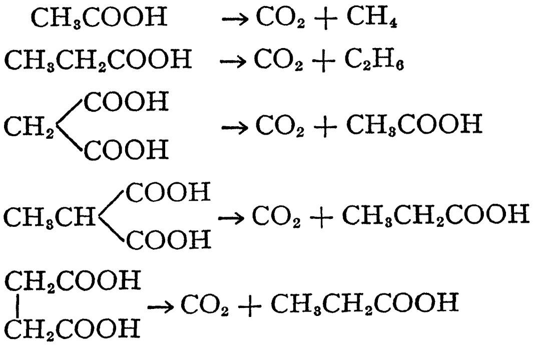
[5] The necessary thermochemical data were taken from the International Critical Tables. The values for the vaporisation of carbon, and the strengths of the H—H and O—O bonds were taken to be 154, 51 and 59 Cal. respectively.

TABLE VIII

Heats of Formation from Gaseous Atoms

	Cal.		Cal.
CH_4 (g)	373.1	 $\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}$ (s)	1115.2
CO (g)	366.		
C_2H_6 (g)	637.5	 $\mathrm{CH_3CH}\Big\langle\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}$ (s)	1377.2
CH_3COOH (g)	743.	 $\begin{matrix}\mathrm{CH_2COOH}\\\vert\\\mathrm{CH_2COOH}\end{matrix}$ (s)	1384.
CH_3CH_2COOH (l)	1009.4		

molecules; the results are shown in Table VIII. It will be seen from this table that none of the reactions,



$$\mathrm{CH_3COOH} \rightarrow \mathrm{CO_2} + \mathrm{CH_4}$$
$$\mathrm{CH_3CH_2COOH} \rightarrow \mathrm{CO_2} + \mathrm{C_2H_6}$$
$$\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix} \rightarrow \mathrm{CO_2} + \mathrm{CH_3COOH}$$
$$\mathrm{CH_3CH}\Big\langle\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix} \rightarrow \mathrm{CO_2} + \mathrm{CH_3CH_2COOH}$$
$$\begin{matrix}\mathrm{CH_2COOH}\\\vert\\\mathrm{CH_2COOH}\end{matrix} \rightarrow \mathrm{CO_2} + \mathrm{CH_3CH_2COOH}$$

involve any appreciable evolution of heat. The explanation of the difficulty may be in the experimental fact that these decompositions occur under the special conditions obtaining in the liquid phase. (See Chapter XIV.)

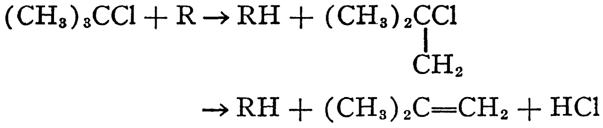
Chlorine Derivatives.—The products predicted by the chain mechanism for these compounds agree fairly well with the products found experimentally.[6] Ethyl chloride probably decomposes chiefly through the chain,

$$\begin{aligned}\mathrm{CH_3CH_2Cl} + \mathrm{R} &\rightarrow \mathrm{RH} + \mathrm{CH_2CH_2Cl}\\ &\rightarrow \mathrm{RH} + \mathrm{CH_2{=}CH_2} + \mathrm{Cl}\end{aligned}$$
$$\mathrm{R} = \mathrm{Cl}$$

---

[6] See Hurd, *Pyrolysis of Organic Compounds,* Chapter VI. Chemical Catalog Co., 1929.

which would give ethylene and hydrochloric acid as the products. The decomposition of tertiary butyl chloride can be represented by only one chain cycle



$$(CH_3)_3CCl + R \rightarrow RH + (CH_3)_2\underset{\substack{|\\ CH_2}}{C}Cl$$
$$\rightarrow RH + (CH_3)_2C{=}CH_2 + HCl$$

yielding isobutylene and hydrochloric acid.[7]

Symmetrical dichlorethane [8] would be expected to decompose through the chain:

$$CH_2ClCH_2Cl + R \rightarrow RH + CH_2ClCHCl$$
$$\rightarrow RH + CH_2{=}CHCl + Cl$$

Vinyl chloride and hydrochloric acid should be the main products of the reaction. Actually Boeseken and Bastet [9] have prepared vinyl chloride by heating ethylene dichloride.

Alkyl Nitrites.—The thermal decomposition of the methyl and ethyl esters of the alkyl nitrites has been studied recently.[10] The main reaction occurring during the decomposition of methyl nitrite conducted at pressures about 100 or 200 mm., is:

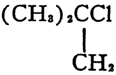
$$CH_3ONO \rightarrow NO + \tfrac{1}{2}\,HCHO + \tfrac{1}{2}\,CH_3OH$$

For ethyl nitrite under the same conditions we have:

$$CH_3CH_2ONO \rightarrow NO + \tfrac{1}{2}\,CH_3CH_2OH + \tfrac{1}{2}\,CH_3CHO$$

Both decompositions are homogeneous and follow a unimolecular law; the activation energies are 36.4 and 37.7 Cal. respectively.

These compounds are especially interesting because the reaction of either one with a free radical should result in the formation of molecules only. Thus a methyl group produced in an atmosphere of methyl nitrite would be expected to react as follows:



[7] This is on the assumption that the radical $(CH_3)_2\underset{\substack{|\\ CH_2}}{C}Cl$ does not decompose into $CH_3CCl{=}CH_2 + CH_3$.

[8] See Sherman and Sun, *J. Am. Chem. Soc.*, **56**, 1096 (1934) for a theoretical discussion of this and similar decompositions.

[9] Boeseken and Bastet, *Rec. trav. chim.*, **32**, 187 (1914).

[10] Steacie and Shaw, *Proc. Roy. Soc.*, **146 A**, 388 (1934); *idem.*, *J. Chem. Physics*, **2**, 345 (1934).

$$\mathrm{CH_3 + CH_3ONO \rightarrow CH_4 + —CH_2ONO}$$

$$\mathrm{—CH_2ONO \rightarrow NO + HCHO}$$

A similar series of reactions would be expected in the case of ethyl nitrite:[11]

$$\mathrm{CH_3 + CH_3CH_2ONO \rightarrow CH_4 + CH_3\overset{|}{C}HONO}$$

$$\mathrm{CH_3\overset{|}{C}HONO \rightarrow CH_3CHO + NO}$$

Thus it can be seen that these compounds could not themselves decompose through a chain mechanism; furthermore, they might be expected to inhibit the decomposition of other compounds that do decompose through a chain.

Actually, it has been found that when pure ethyl nitrite is passed[12] at low pressures through a tube heated in the range 400-600°, no removal of metallic mirrors occurs, although the nitrite had been decomposed. According to the foregoing reasoning this result is to be expected, since the production of a free radical by such primary reactions as

$$\begin{aligned}\mathrm{CH_3CH_2ONO} &\rightarrow \mathrm{NO + CH_3CH_2O—} \quad \text{or}\\ &\rightarrow \mathrm{NO + HCHO + CH_3—}\end{aligned}$$

would be followed by reaction of the radicals with undecomposed ethyl nitrite to yield molecules only. It was found, however, that when the ethyl nitrite is diluted with an inert gas, the rate of the bimolecular reaction of the radicals with the ethyl nitrite can be reduced to negligible proportions and mirror removal occurs with great readiness. The fragments were found to be methyl groups.

Ethylene nitrite has not been investigated but it might be expected to show a similar behavior and break up into molecules only; furthermore it should be expected to give no mirror removal either with the pure vapor or when diluted with an inert gas. Thus the primary decomposition,

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[11] We have omitted consideration of the reaction $\mathrm{R + CH_3CH_2ONO \rightarrow RH + —CH_2CH_2ONO}$, because the reaction of the free radical with the more loosely bound secondary hydrogen atom in the α position to the —ONO group probably predominates. Furthermore, the decomposition $\mathrm{CH_2CH_2ONO \rightarrow NO + CH_2CH_2O \rightarrow NO + CH_3CHO}$ would lead to the same final result.

[12] F. O. Rice and Edward L. Rodowskas, Unpublished work. These results are for mirrors placed 2–3 cm. from the furnace. Mirrors closer than this are slowly removed.

$$ONOCH_2CH_2ONO \rightarrow —OCH_2CH_2ONO + NO$$

should be followed by the reaction,

$$—OCH_2CH_2ONO \rightarrow NO + 2HCHO$$

which probably requires only a very small activation energy.

Aliphatic Azocompounds.—The decomposition of azomethane has been investigated by Ramsperger,[13] who found that the overall decomposition could be represented by the equation $CH_3N{=}NCH_3 \rightarrow C_2H_6 + N_2$. This seems to exclude the possibility of a chain mechanism since a primary step,

$$CH_3N{=}NCH_3 \rightarrow CH_3 + CH_3N{=}N—,$$

followed by reaction of the methyl groups with azomethane would yield quite other products.[14] Further evidence that the decomposition of azomethane is not a chain reaction has been obtained by introducing[15] ethyl radicals (from lead tetraethyl) into azomethane at 275°. The measured and calculated rate of decomposition of the mixture of lead tetraethyl and azomethane were the same, indicating that, at least under the conditions of the experiment, there is no reaction between ethyl radicals and azomethane. Since the fragments formed in the thermal decomposition of azomethane readily remove metallic mirrors[16] we may conclude that in all probability the decomposition consists of the primary separation of methyl groups from the molecule followed by their recombination to form ethane.

The decomposition of azo*iso*propane probably follows a somewhat similar course since the overall reaction can be represented[17] (to the extent of about 85%) by the equation,

$$(CH_3)_2CHN{=}NCH(CH_3)_2 \rightarrow C_6H_{14} + N_2$$

At low pressures the fragments from azo*iso*propane readily remove mirrors.[16b] Identification of the fragments has not yet been accomplished; it should, however, be of special interest since it would furnish some information regarding the relative activation energies of the possible reactions,

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[13] Ramsperger, *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927).

[14] It is also necessary to exclude the skeleton breaking reaction $CH_3 + CH_3N{=}NCH_3 \rightarrow C_2H_6 + CH_3N{=}N—$. See p. 81.

[15] Leermakers, *J. Am. Chem. Soc.*, **55**, 4508 (1933).

[16] (a) Leermakers, *J. Am. Chem. Soc.*, **55**, 3499 (1933); (b) Rice and Evering, *ibid.*, **55**, 3898 (1933).

[17] Ramsperger, *J. Am. Chem. Soc.*, **50**, 714 (1928).

$$CH_3CHCH_3 \rightarrow CH_3CH_2CH_2\text{—}\ \text{and}$$

$$CH_3CHCH_3 \rightarrow CH_3CH{=}CH_2 + H$$

and their relation to the primary dissociation,

$$(CH_3)_2CHN{=}NCH(CH_3)_2 \rightarrow CH_3CHCH_3 + \text{—}N{=}NCH(CH_3)_2$$

which might be expected to have an activation energy of 41 Cal., which is the measured value of the overall reaction.

CHAPTER XII

LARGER MOLECULES

In some special cases, the theory of free radicals predicts an extremely simple course for the decomposition of some of the higher members of the paraffin hydrocarbon series. For example, according to this theory the decomposition of the octane, hexamethyl ethane, should occur through one chain cycle, which produces only isobutane and hydrogen:

$$\begin{aligned} \text{A}\quad (CH_3)_3C{-}C(CH_3)_3 + R &\rightarrow RH + (CH_3)_3C{-}C(CH_3)_2CH_2{-} \\ &\rightarrow RH + C_4H_8{-}\text{iso} + (CH_3)_3C{-} \\ &\rightarrow RH + C_4H_8{-}\text{iso} + C_4H_8{-}\text{iso} + H \end{aligned}$$

The decomposition of hexadecane, $C_{16}H_{34}$, may be selected as typical for long unbranched hydrocarbon chains. We shall consider only the various chain mechanisms since the primary dissociation by rupture of C—C bonds is relatively unimportant so far as the final products are concerned. It is evident, in the first place, since the hydrocarbon is symmetrical, that there will be eight chain cycles according as a hydrogen atom is removed from one of the eight carbon atoms numbered 1 to 8 in the molecule:

$$\begin{array}{cccccccccccccccc} CH_3 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_3 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 \end{array}$$

The first cycle, A_1, comes from the removal of one of the six terminal hydrogen atoms, with formation of the normal radical $C_{16}H_{33}$. If the decomposition is carried out at atmospheric pressure or lower and at high temperatures the unimolecular decomposition of this radical is facilitated so that it should yield $7\,C_2H_4 + CH_3CH_2$. On the other hand, under conditions of high pressure and low temperature the bimolecular reaction between the radical and the surrounding molecules will be favored, so that after one molecule of ethylene has broken off the radical $C_{14}H_{29}$ will probably react with the surrounding molecules to give the paraffin hydrocarbon[1] $C_{14}H_{30}$.

The different chain cycles which may be expected to take place under conditions of low pressure and high temperature, when the large alkyl radicals first produced break down into methyl or ethyl groups, may be summarized as follows:[1a]

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[1] There is also the possibility that the large radicals formed in the chain process decompose to some extent into naphthene hydrocarbons such as cyclopentane and cyclohexane and smaller radicals (see p. 85). This process would be favored by low temperature and dilution of the substrate hydrocarbon by an inert gas.

$A_1 \quad C_{16}H_{34} \rightarrow 7\,C_2H_4 + C_2H_6$

$A_2 \quad C_{16}H_{34} \rightarrow C_3H_6 + 6\,C_2H_4 + CH_4$

$A_3 \quad C_{16}H_{34} \rightarrow C_4H_8\text{—}1$[1a] $+ 5\,C_2H_4 + C_2H_6$

$A_4 \quad C_{16}H_{34} \rightarrow 0.5\,C_5H_{10}\text{—}1 + 2.5\,C_2H_4 + 0.5\,CH_4 + 0.5\,C_2H_6 + 0.5\,C_{14}H_{28}\text{—}1$

$A_5 \quad C_{16}H_{34} \rightarrow 0.5\,C_6H_{12}\text{—}1 + 2\,C_2H_4 + 0.5\,C_2H_6 + 0.5\,C_2H_4 + 0.5\,CH_4 + 0.5\,C_{13}H_{26}\text{—}1$

$A_6 \quad C_{16}H_{34} \rightarrow 0.5\,C_7H_{14}\text{—}1 + 2\,C_2H_4 + 0.5\,CH_4 + 0.5\,C_2H_4 + 0.5\,C_2H_6 + 0.5\,C_{12}H_{24}\text{—}1$

$A_7 \quad C_{16}H_{34} \rightarrow 0.5\,C_8H_{16}\text{—}1 + 1.5\,C_2H_4 + 0.5\,C_2H_6 + C_2H_4 + 0.5\,CH_4 + 0.5\,C_{11}H_{22}\text{—}1$

$A_8 \quad C_{16}H_{34} \rightarrow 0.5\,C_9H_{18}\text{—}1 + 1.5\,C_2H_4 + 0.5\,CH_4 + C_2H_4 + 0.5\,C_2H_6 + 0.5\,C_{10}H_{20}\text{—}1$

A second set of equations represents the decomposition under conditions of high pressure and low temperature, when the large radicals first formed undergo only one step of further decomposition:

$A_1 \quad C_{16}H_{34} \rightarrow C_2H_4 + C_{14}H_{30}$

$A_2 \quad C_{16}H_{34} \rightarrow C_3H_6 + C_{13}H_{28}$

$A_3 \quad C_{16}H_{34} \rightarrow C_4H_8\text{—}1 + C_{12}H_{26}$

$A_4 \quad C_{16}H_{34} \rightarrow 0.5\,C_5H_{10}\text{—}1 + 0.5\,C_{11}H_{24} + 0.5\,C_2H_6 + 0.5\,C_{14}H_{28}\text{—}1$

$A_5 \quad C_{16}H_{34} \rightarrow 0.5\,C_6H_{12}\text{—}1 + 0.5\,C_{10}H_{22} + 0.5\,C_3H_8 + 0.5\,C_{13}H_{26}\text{—}1$

$A_6 \quad C_{16}H_{34} \rightarrow 0.5\,C_7H_{14}\text{—}1 + 0.5\,C_9H_{20} + 0.5\,C_4H_{10} + 0.5\,C_{12}H_{24}\text{—}1$

$A_7 \quad C_{16}H_{34} \rightarrow 0.5\,C_8H_{16}\text{—}1 + 0.5\,C_8H_{18} + 0.5\,C_5H_{12} + 0.5\,C_{11}H_{22}\text{—}1$

$A_8 \quad C_{16}H_{34} \rightarrow 0.5\,C_9H_{18}\text{—}1 + 0.5\,C_7H_{16} + 0.5\,C_6H_{14} + 0.5\,C_{10}H_{20}\text{—}1$

Assuming equal probabilities for the sixteen possible reactions, the decomposition may be summarised as shown in Table VIII.

[1a] All the olefins produced according to this scheme would be expected to have the double bond at the end of the chain. This has been indicated by the symbol —1.

TABLE VIII

THERMAL DECOMPOSITION OF HEXADECANE, $C_{16}H_{34}$

	CH_4	C_2H_6	C_3H_8	C_nH_{2n+2}	C_2H_4	C_3H_6	C_4H_8	C_nH_{2n}
Low Press. %...	7.7	9.9	—	—	67.0	2.2	2.2	11.0
High Press. %...	—	3.1	3.1	43.7	6.2	6.2	6.2	31.2

The upper line represents the decomposition under conditions that favor the decomposition of the large radicals, that is, at high temperatures and at atmospheric pressure or lower. It will be seen that under these conditions 85% of the molecules produced consist of methane, ethane, and ethylene. The remaining 15% is an equimolecular mixture of olefins from C_3 to C_{14}; these are all straight chain mono-olefins with the double bond at the end of the chain. On the other hand, when the decomposition is carried out under conditions that favor the reaction between the large free radicals and the surrounding hydrocarbon molecules, no methane appears and less than 10% of ethane and ethylene; instead there is produced 43% of a mixture of normal paraffin hydrocarbons from C_4 to C_{11} inclusive and 31.2% of straight chain mono-olefins, again with the double bond at the end of the chain.

The decomposition of hexadecane has been extensively studied by Gault and Hessel;[2] in most of their experiments they obtained over 2 moles of gaseous products from each mole of hydrocarbon passed through the furnace, so that it is hardly possible to interpret this part of the work, since it must involve considerable degradation of the primary products of the decomposition. However, the authors describe two experiments in which comparatively small fractional decompositions occurred. The gaseous products from 100 grams were

	% H	% Saturated	% Unsaturated
615° C.; 1500 cc. gas	2	30	68
470° C.; 180 cc. gas	0	72	28

These figures compare reasonably well with the calculated values for the relative amounts of the lower hydrocarbons. Furthermore, the liquid decomposition products at the higher temperature contained considerably more unsaturated products than at the lower temperature, and distillation with cuts at 20° intervals yielded a series of approximately equal fractions from 80° to 283°, which is the boiling point of the hexadecane, all of which is also in substantial agreement with the calculations.

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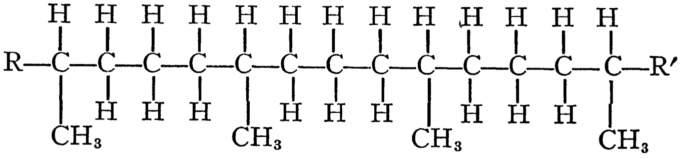
[2] Gault and Hessel, *Ann. chim.*, **2**, 319 (1924).

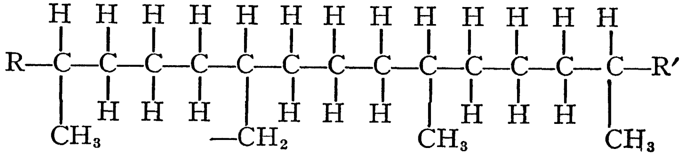
High molecular weight hydrocarbons with side chains, on the other hand, give quite different results, particularly when the side-chains recur at definite intervals. It seems to be a characteristic of many naturally occurring substances that the molecule consists of a succession of repeating units; thus, proteins contain the recurring group —$CONH_2CHR$—; terpenes, rubber, and many vegetable coloring matters such as lycopin, the red coloring matter of tomatoes, are unsaturated hydrocarbons built up of a succession of isoprene units. The products of the thermal decomposition of such compounds should be determined almost entirely by the characteristic unit. Of course, this fact has been familiar to chemists since a long time and has been frequently applied in connection with problems concerning the structure of complicated molecules.[3]

It is of some interest to examine the products to be expected when saturated hydrocarbons containing various recurring units are decomposed at high temperatures and low pressures.[4] The decomposition of a long chain paraffin hydrocarbon containing a recurring isoprene skeleton will be worked out in detail and it will be shown that ethylene and propylene in a 1 : 1 ratio would be expected to predominate in the products. The hydrocarbon may be written as follows, allowing R and R′ to represent the continuation of the chain:



$$\begin{array}{ccccccccccccccc}
 & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & \\
\mathrm{R}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{R'} \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & \\
 & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} &
\end{array}$$

Such a molecule should decompose according to a chain mechanism; the removal of a hydrogen atom will produce for example:



$$\begin{array}{ccccccccccccccc}
 & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & \\
\mathrm{R}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{R'} \\
 & | & | & | & | & | & | & | & | & | & | & | & | & | & \\
 & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & -\mathrm{CH_2} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} &
\end{array}$$

This radical will then decompose, forming

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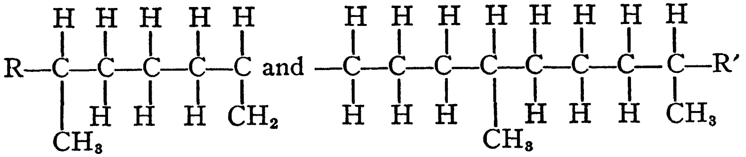
[3] See Kühn and Winterstein, *Ber.*, **65 B**, 1873 (1932).

[4] Always with the assumption that we are dealing with only a small fractional decomposition, in the gaseous state.



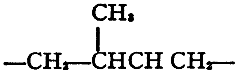
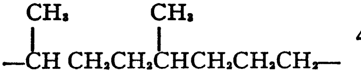
$$R-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_2}{\overset{H}{C}}\text{ and }-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-R'$$

This latter radical breaks down to produce many molecules of ethylene and propylene in a 1 : 1 ratio, until finally a methyl or an ethyl group is left which will react with a new molecule of the original hydrocarbon to continue the chain. The result will be the same no matter which hydrogen atom of the original hydrocarbon is first removed. Ethylene and propylene should predominate among the products; they should be accompanied by small quantities of methane, ethane and higher olefins; if the hydrocarbon has a sufficiently long chain (C_{20} or more) the complications at the two ends of the chain may be neglected. Similar calculations may be made for other saturated hydrocarbons containing recurring units; the results for some of these are shown in Table IX.

TABLE IX

Lower Olefins (C_2 to C_4) Produced in the Decomposition of High Molecular Weight Substances Containing a Recurring Unit

Unit	% C_2H_4	C_3H_6	C_4H_8—1	C_4H_8—2
$-\overset{CH_3}{\overset{\vert}{C}}H-$	—	—	—	100
$-\overset{CH_3}{\overset{\vert}{C}}HCH_2-$	—	100	—	—
$-\overset{CH_3}{\overset{\vert}{\overset{CH_2}{\overset{\vert}{C}}}}HCH_2-$	15	—	85	—
$-CH_2\overset{CH_3}{\overset{\vert}{C}}H-\overset{CH_3}{\overset{\vert}{C}}H-CH_2-$	19	62	—	19
$-\overset{CH_3}{\overset{\vert}{C}}H-\overset{CH_3}{\overset{\vert}{C}}H-CH_2-$	—	66.6	—	33.3
$-CH_2-\overset{CH_3}{\overset{\vert}{C}}H-CH_2$	33.3	66.6	—	—

Unit	% C_2H_4	C_3H_6	C_4H_8—1	C_4H_8—2
 $-CH_2-\overset{\overset{CH_3}{\mid}}{C}HCH\ CH_2-$	50	50	—	—
 $-\overset{\overset{CH_3}{\mid}}{C}H\ CH_2CH_2\overset{\overset{CH_3}{\mid}}{C}HCH_2CH_2CH_2-$	45	55	—	—

Non-volatile Organic Compounds.—The foregoing considerations may apply to organic liquids and solids as well as to gases, so long as the substance under investigation meets one requirement: it must have a vapor pressure of at least a few mm. at some temperature below its decomposition point. The decomposition can then occur in the vapor state according to the free radical mechanisms described in the foregoing chapters. On the other hand, there are many organic compounds that cannot be distilled even in the highest vacuum at any temperature below their decomposition point. It is obvious that the destructive distillation of a non-volatile solid gives relatively little opportunity for chain formation; this is especially the case if the decomposition is conducted in a high vacuum, because the products are then rapidly swept away from the hot surface and should not suffer further degradation to any appreciable extent. Therefore it is to be expected that in such a case the primary rupture will determine the nature of the products.

When the constitution of a large molecule is such that decomposition occurs in the range 250—400°, the large radicals formed in the primary rupture may be expected to decompose successively into molecules, by ring formation (see p. 85), instead of into open chain compounds. The products of the decomposition may then be predicted by making the following assumptions: (1) Rings containing 5 members form most easily, rings containing 6 or 7 members form somewhat less easily, and rings containing 3, 4, 8, 9, 10, 11, 12 or 13 members do not form readily. Rings containing 15 or more atoms form very readily.[5] (2) When ring formation occurs, the new bond formed must be at least approximately as strong as the bond broken. Ring formation is favored at a point where the new bond formed is stronger than the bond broken. (3) If there is an atom in the chain (like S or O) with no attached hydrogen atom or if there is a doubly bound C atom with only one hydrogen atom attached, ring formation is favored at these points, because the fewer attached hydrogen atoms should greatly diminish the steric hindrance. If for some reason the ring cannot form at these points the adjoining C atoms are preferred to others in the chain. The application of these rules to various high molecular weight substances will now be considered and the calculated results will be compared with those obtained experimentally when these are available.

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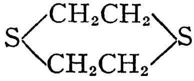
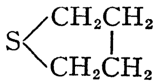
[5] Carothers and Hill, *J. Am. Chem. Soc.*, **55**, 5043 (1933).

A great variety of high molecular weight substances are polymers, that is they are characterized by the fact that a group of atoms forms a recurring unit. The foregoing rules can be illustrated by the thermal decomposition of some unsaturated long chain polymers containing sulfur in the chain which have recently been studied in some detail.[6] Since the relative strengths of the bonds in such molecules may unquestionably be represented as C—C >> C—S >> S—S, speculation as to which bonds break is reduced to a minimum. We have assumed that the primary rupture occurs only at C—S bonds and that the probability of rupture is the same for all of these bonds.

Polymer A. $R(CH_2CH_2S)_nR'$.

A_1 $RCH_2CH_2S'CH_2CH_2SCH_2CH_2S'CH_2CH_2SCH_2CH_2S'$—

A_2 $RCH_2CH_2{}'SCH_2CH_2SCH_2CH_2{}'SCH_2CH_2SCH_2CH_2{}'$—

The strokes above the radicals mark the points at which rupture should occur according to the foregoing rules. Thus, this polymer consists of the recurring unit $—CH_2CH_2S—$ and accordingly there are two possibilities of rupture, producing respectively radicals A_1 and A_2. The decomposition of the radical A_1 can yield only the six membered ring 1, 4–dithiane,  $S\begin{smallmatrix}\diagup CH_2CH_2\diagdown \\ \diagdown CH_2CH_2\diagup\end{smallmatrix}S$: formation of a five membered ring is forbidden by rule (2) since a C—C bond must be broken but only a C—S bond is made. Similarly a seven membered ring would require the rupture of a C—S bond and the formation of the much weaker S—S bond. Similarly the decomposition of the radical A_2 also yields only the six membered ring dithiane. There is the possibility that the first step in the decomposition of the radical A_2 would result in the formation of tetramethylene sulfide  $S\begin{smallmatrix}\diagup CH_2CH_2 \\ | \\ \diagdown CH_2CH_2\end{smallmatrix}$ since this would require the formation a C—C bond with rupture of the weaker C—S bond; however it seems likely that the absence of steric hindrance at the S atom (Rule 3) would favor the formation of the six membered ring, and in any case after one molecule of tetramethyl sulfide had broken off, radical A_1 would result.

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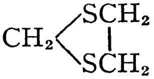
[6] Meadow and Reid, *J. Am. Chem. Soc.*, 56, 2177 (1934). The decomposition was effected by heating at about 200° for several hours in a high vacuum.

The decomposition of polymer A should yield, therefore, chiefly 1, 4–dithiane.[7] Experimentally 1, 4–dithiane was obtained in 40–60% yield and was the only product isolated.

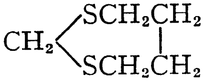
Polymer B. $R(CH_2CH_2SCH_2S)_nR'$.

B_1 $R'CH_2CH_2SCH_2S'CH_2CH_2SCH_2S'CH_2CH_2SCH_2S'$—
B_2 $RCH_2CH_2SCH_2'SCH_2CH_2SCH_2'SCH_2CH_2SCH_2'$—
B_3 $RCH_2CH_2S'CH_2SCH_2CH_2S'CH_2SCH_2CH_2S'$—
B_4 $RCH_2CH_2'SCH_2SCH_2CH_2'SCH_2SCH_2CH_2'$—.

This polymer consists of the recurring unit —$CH_2CH_2SCH_2S$— and accordingly there are four possibilities of rupture producing respectively the radicals B_1, B_2, B_3, and B_4. From application of the foregoing rules it follows that nothing except 1, 3–dithiolane  $CH_2{<}\begin{array}{l}SCH_2\\ \;\;|\\ SCH_2\end{array}$ should be formed in this decomposition. Experimentally, a 30% yield was obtained and no other product was isolated.

Polymer C. $R(CH_2CH_2SCH_2CH_2CH_2S)_nR'$.

C_1 $R'CH_2CH_2SCH_2CH_2CH_2S'CH_2CH_2SCH_2CH_2CH_2S'$—
C_2 $RCH_2CH_2SCH_2CH_2CH_2'SCH_2CH_2SCH_2CH_2CH_2'$—
C_3 $RCH_2CH_2S'CH_2CH_2CH_2SCH_2CH_2S'$—
C_4 $RCH_2CH_2'SCH_2CH_2CH_2SCH_2CH_2'$—.

This polymer has again four possibilities of rupture, producing respectively one of the radicals C_1 to C_4. According to the foregoing rules neither five nor six membered rings are possible in the decomposition of any of these four radicals. The seven membered ring  $CH_2{<}\begin{array}{l}SCH_2CH_2\\ \qquad\;\;|\\ SCH_2CH_2\end{array}$ should be the only product. Actually 5–10% of this compound was found experimentally but it was reported accompanied by an approximately equal amount of 1, 4 dithiane which cannot be accounted for according to the theory.

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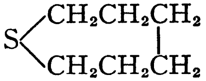
[7] Large sulfur-containing rings of 15 or more members would also be expected to be present in the residue of this and the other polymers. This point was not investigated experimentally.

Polymer D. $R(CH_2CH_2CH_2S)_nR'$.

D_1 $RCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2S''$—

D_2 $RCH_2CH_2CH_2S''CH_2CH_2CH_2SCH_2CH_2CH_2'$—.

Here the double strokes indicate that point beyond which further decomposition cannot be predicted by use of the rules given above. Thus, the radical D_1 can only decompose by formation of an eight membered ring which is forbidden by rule 1. Similarly the radical D_2 is transformed into radical D_1 by splitting off  and can then not decompose further in this way. It is not possible therefore on the basis of these rules to predict the products of decomposition. Actually nothing definite could be isolated experimentally.

Polymer E. $R(CH_2CH_2SO_2CH_2CH_2SCH_2CH_2S)_nR'$.

E_1 $R'CH_2CH_2SO_2CH_2CH_2S'CH_2CH_2SCH_2CH_2SO_2'CH_2CH_2SCH_2CH_2S'$—

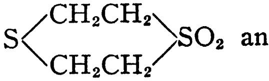
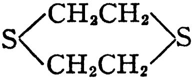
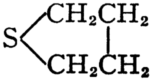
E_2 $R'CH_2CH_2SO_2CH_2CH_2S'CH_2CH_2SCH_2CH_2SO_2'CH_2CH_2SCH_2CH_2'$—

E_3 $RCH_2CH_2SO_2'CH_2CH_2SCH_2CH_2S'CH_2CH_2SO_2CH_2CH_2S'$—

E_4 $RCH_2CH_2SO_2'CH_2CH_2SCH_2CH_2'SCH_2CH_2SO_2CH_2CH_2'$—

E_5 $R'CH_2CH_2SO_2CH_2CH_2S'CH_2CH_2SCH_2CH_2SO_2'$—

E_6 $RCH_2CH_2SO_2CH_2CH_2'SCH_2CH_2SCH_2CH_2'$—.

The primary rupture of this polymer can occur in six different ways, yielding respectively the radicals E_1 to E_6. The radical E_1 should decompose yielding the six membered rings  and  in the proportion of 2: 1. The radicals E_3, E_5 and E_6 decompose in an exactly similar manner yielding the same products. The radical E_2, according to the foregoing rules, may be expected to yield first a molecule of tetramethylene sulfide  and then to decompose in the same way as E_1. Similarly, the radicals E_4 and E_6 should give the same products as E_1 accompanied in each case by one molecule of tetramethylene sulfide.

The products of the decomposition should therefore be chiefly 1, 4 dithiane and its monosulfone in the proportion of 1: 2, accompanied by a small proportion of tetramethylene sulfide. Experimentally 20%

of the monosulfone was recovered and 10–15% of 1, 4–dithiane. Nothing else was isolated.

Polymer F. $R(CH_2CH_2OCH_2CH_2SCH_2CH_2S)_nR'$.

F_1 $RCH_2CH_2OCH_2CH_2SCH_2CH_2S''$—

F_2 $RCH_2CH_2OCH_2CH_2'SCH_2CH_2SCH_2CH_2'OCH_2CH_2SCH_2CH_2'$—

F_3 $RCH_2CH_2OCH_2CH_2SCH_2CH_2S''CH_2CH_2OCH_2CH_2S'$—

F_4 $RCH_2CH_2'OCH_2CH_2SCH_2CH_2'SCH_2CH_2OCH_2CH_2'$—.

The radical F_1 cannot decompose to form five, six or seven membered rings; similarly, after the radical F_3 loses one molecule of 1, 4–thioxane it is identical with F_1 and cannot decompose further to give rings. On the other hand radicals F_2 and F_4 decompose to give the same products, namely the two six membered rings 1, 4–thioxane and 1, 4 dithiane in the proportion 2 : 1. Experimentally, a 15–20% yield of 1, 4–thioxane and a 5–10% yield of 1, 4–dithiane was obtained.

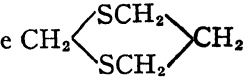
Polymer G. $R(CH_2CH_2CH_2SCH_2S)_nR'$.

G_1 $R'CH_2CH_2CH_2SCH_2S'CH_2CH_2CH_2SCH_2S'$—

G_2 $RCH_2CH_2CH_2SCH_2'SCH_2CH_2CH_2SCH_2'$—

G_3 $RCH_2CH_2CH_2S'CH_2SCH_2CH_2CH_2S'$—

G_4 $RCH_2CH_2CH_2'SCH_2SCH_2CH_2CH_2'$—.

All the radicals produced in the primary decomposition should decompose readily into the six membered ring 1, 3 dithiane  $CH_2\langle {SCH_2 \atop SCH_2} \rangle CH_2$ which should therefore be the chief product of the decomposition. Experimentally it was obtained in 30–40% yield and was the only product isolated.

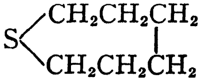
Polymer H. $R(CH_2CH_2SCH_2CH_2CH_2CH_2CH_2CH_2S)_nR'$.

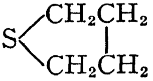
H_1 $RCH_2CH_2SCH_2CH_2CH_2CH_2CH_2CH_2SCH_2CH_2S''CH_2CH_2CH_2CH_2CH_2CH_2S'$

H_2 $RCH_2CH_2''SCH_2CH_2CH_2CH_2'CH_2CH_2SCH_2CH_2'SCH_2CH_2CH_2CH_2CH_2CH_2'$—

H_3 $RCH_2CH_2SCH_2CH_2CH_2CH_2CH_2CH_2SCH_2CH_2S''$—

H_4 $RCH_2CH_2'SCH_2CH_2CH_2CH_2'CH_2CH_2SCH_2CH_2'$—.

The radical H_3 cannot decompose by ring formation nor can the radical H_1 decompose further after the ring  $S\langle {CH_2CH_2CH_2 \atop CH_2CH_2CH_2} \rangle$ is broken off.

On the other hand the radicals H_2 and H_4 should decompose to give tetramethylene sulfide  as the chief product. This is not in agreement with experiment since 1, 4 dithiane (10% yield) was the only product isolated.

Polymer I. $\mathrm{R(CH_2CH_2CH_2SCH_2CH_2CH_2S)_{\mathit{n}}R'}$.

$\mathrm{I_1}$ $\mathrm{RCH_2CH_2CH_2SCH_2CH_2CH_2CH_2SCH_2CH_2CH_2S''CH_2CH_2CH_2CH_2S}$—

$\mathrm{I_2}$ $\mathrm{RCH_2CH_2CH_2S''CH_2CH_2CH_2CH_2SCH_2CH_2'CH_2S\,CH_2CH_2CH_2'CH_2S}$
$\mathrm{CH_2CH_2CH_2'SCH_2CH_2CH_2CH_2'}$—

$\mathrm{I_3}$ $\mathrm{RCH_2CH_2CH_2SCH_2CH_2CH_2CH_2SCH_2CH_2CH_2S''}$—

$\mathrm{I_4}$ $\mathrm{RCH_2CH_2CH_2S''CH_2CH_2CH_2CH_2SCH_2CH_2'CH_2S\,CH_2CH_2CH_2'}$—.

The radicals I_1, I_2 and I_4 decompose to some extent until the radical I_3 is formed which does not decompose further by ring formation. According to this scheme tetramethylene sulfide and hexamethylene sulfide should be formed in poor yield in the proportion 3: 1 respectively. Tetramethylene sulfide only has been reported experimentally (10% yield).

Polymer J. $\mathrm{R(CH_2CH_2CH_2SCH_2CH_2CH_2CH_2CH_2S)_{\mathit{n}}R'}$.

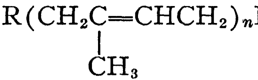
$\mathrm{J_1}$ $\mathrm{RCH_2CH_2CH_2SCH_2CH_2CH_2CH_2CH_2SCH_2CH_2CH_2S''CH_2CH_2CH_2CH_2CH_2S'}$—

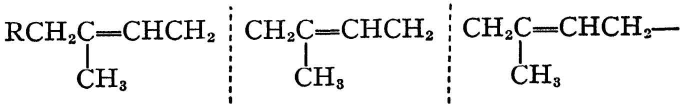
$\mathrm{J_2}$ $\mathrm{RCH_2CH_2CH_2'SCH_2CH_2CH_2CH_2'CH_2SCH_2CH_2CH_2''S\,CH_2CH_2CH_2CH_2CH_2'}$—

$\mathrm{J_3}$ $\mathrm{RCH_2CH_2CH_2SCH_2CH_2CH_2CH_2CH_2SCH_2CH_2CH_2S''}$—

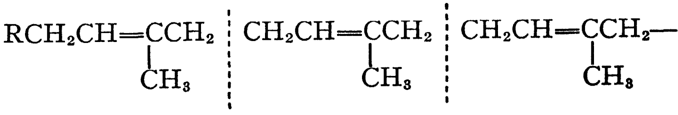
$\mathrm{J_4}$ $\mathrm{RCH_2CH_2CH_2'SCH_2CH_2CH_2CH_2'CH_2SCH_2CH_2CH_2''}$—.

The radical J_1 breaks off pentamethylene sulfide and leaves a radical identical with J_3 which cannot decompose further. The radicals J_2 and J_4 decompose to give chiefly tetramethylene sulfide which should be the main product of the reaction. However Meadow and Reid[6] do not report any tetramethylene sulfide but only pentamethylene sulfide in 15–20% yield.

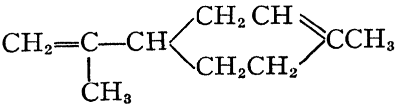
From the chemical standpoint the simplest example of a high molecular weight polymer is a hydrocarbon containing recurring double bonds: the rubber hydrocarbon may be taken as an example of this type of structure. Following the preceding methods, the rubber molecule may be written  $\mathrm{R(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2)_{\mathit{n}}R'}$; it should decompose at the weak C—C bond, which is in the beta position to the double bond, producing the two radicals:

I 

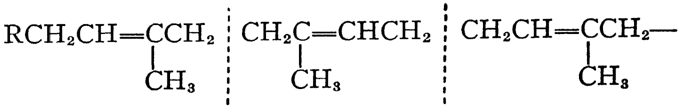
$$RCH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2 \;\vdots\; CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2 \;\vdots\; CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2-$$

II 

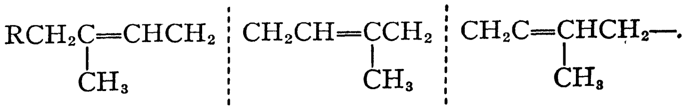
$$RCH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2 \;\vdots\; CH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2 \;\vdots\; CH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2-.$$

The vertical broken lines mark the positions of the weak bonds in the radicals. It is clear that the decomposition of radical I into the molecule dipentene  $CH_2=\underset{CH_3}{\underset{|}{C}}-CH\begin{smallmatrix}\diagup CH_2CH\diagdown\!\!\diagdown \\ \diagdown CH_2CH_2\diagup\end{smallmatrix}CCH_3$ agrees best with the foregoing rules. In the first place a six membered ring is formed, in the second place it forms at a point of minimum steric hindrance, and in the third place the bond broken is the weakest in the hydrocarbon chain. On the other hand, formation of either a five or seven membered ring involves breaking a strong C—C bond as well as formation of the 5 membered ring at a point of maximum steric hindrance. The same considerations apply to the decomposition of radical II and consequently we should expect that the decomposition of the rubber hydrocarbon in a high vacuum would yield chiefly dipentene. Experimentally[8] dipentene is found to be the chief product, accompanied by some isoprene; possibly the isoprene is a secondary product, formed by decomposition of the dipentene.

It is interesting to consider the decomposition of an isoprene polymer in which there is a random distribution of the units instead of the oriented structure of the rubber molecule. We would have then to consider the decomposition of such radicals as:

III  and

$$RCH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2 \;\vdots\; CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2 \;\vdots\; CH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2- \text{ and}$$

IV 

$$RCH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2 \;\vdots\; CH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2 \;\vdots\; CH_2C=\underset{CH_3}{\underset{|}{C}}HCH_2-.$$

Both of these would be expected to yield the same terpene hydrocarbon having the formula

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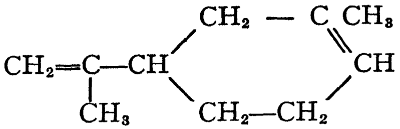
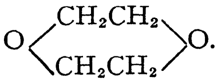
[8] See Midgley and Henne, *J. Am. Chem. Soc.*, **51**, 1215 (1929).



An equimolecular mixture of this hydrocarbon and dipentene should result from the pyrolysis of a polymer consisting of isoprene units with a random orientation.

The essential factor for bringing about ring formation in the decomposition of these high molecular weight polymers is the presence of successive points of weakness in the molecule through some peculiarity in the structure of the recurring unit. This weakness should be sufficiently great so that decomposition of the compound occurs in the low temperature range 250–400°; under these conditions the decomposition of the large radicals into rings is favored, whereas decomposition at higher temperatures should result in the decomposition of the large radicals into unsaturated open chain compounds. (See p. 79.) The decomposition of the polymer $R(CH_2CH_2O)_nR'_1$ may be used to exemplify the two methods of decomposition. The C—C bond is probably slightly weaker than the C—O bond, so that the primary decomposition should yield the radical

$$RCH_2'CH_2O'CH_2CH_2'OCH_2'CH_2O'CH_2CH_2'OCH_2'—$$

The high temperature decomposition into open chain compounds is represented in the above formula in which the strokes mark the bonds at which cleavage should occur; formaldehyde and ethylene in the proportion of 2 : 1 should be the only products. On the other hand, the low temperature decomposition should yield only the six membered ring dioxane  $O\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle O$. Experiments[9] on the decomposition of this polymer at 320–330° and atmospheric pressure yielded volatile compounds among which acetaldehyde and acrolein were identified. Possibly these compounds were produced in secondary decompositions and would not occur if the decomposition were conducted at very low pressures. All the bonds in this and similar polymers would be expected to be fairly strong, that is without pronounced weakness at any one point; it seems possible therefore that they are sufficiently stable that their decomposition points lie in the range in which decomposition into open chain compounds is preferred.

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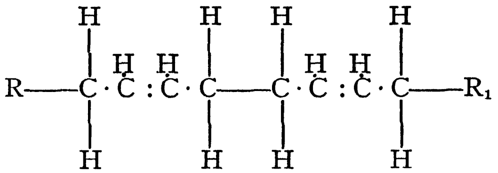
[9] Staudinger and Schweitzer, *Ber.*, 62, 2395 (1929).

On the other hand, the introduction of elements such as sulphur or nitrogen into the recurring unit causes weakness at the C—S and C—N bonds, respectively; the decomposition of such polymers has already been illustrated in detail for some sulphur polymers.

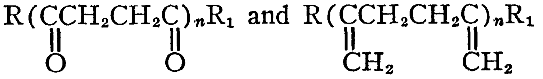
Furthermore, introduction of a double bond in the recurring unit of a polymer causes weak points in positions contiguous to this bond. This may be represented as:



$$R\text{———}\overset{H}{\underset{H}{C}}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{\underset{H}{C}}\text{———}\overset{H}{\underset{H}{C}}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{\underset{H}{C}}\text{———}R_1$$

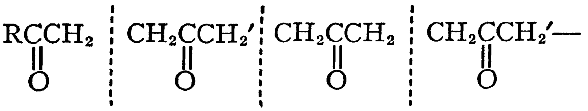
in which the points represent strong bonds and the long strokes represent weak bonds. These weak bonds not only bring about the primary decomposition at a lower temperature and thus favor ring formation but also their position to a large extent determines the character of the products.

It is also possible to introduce weakness at recurring points in the chain of a polymer in an indirect manner, namely by attaching an unsaturated side chain at definite intervals; the influence of this unsaturated group is frequently to weaken what would otherwise be a normal C—C bond. As examples we might consider polymers having the formulas:

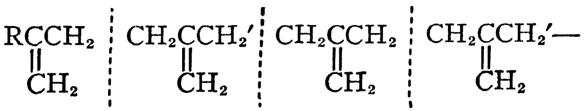


$$R(\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C})_nR_1 \text{ and } R(\underset{\overset{\|}{CH_2}}{C}CH_2CH_2\underset{\overset{\|}{CH_2}}{C})_nR_1$$

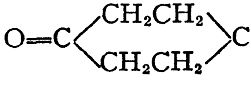
The thermal rupture of these molecules would be expected to yield the radicals:

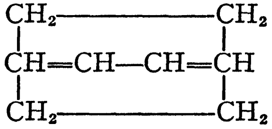
(1)  and

$$R\underset{\overset{\|}{O}}{C}CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}CH_2' \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}CH_2'\text{—}$$

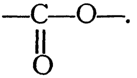
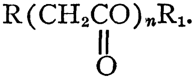
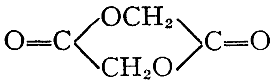
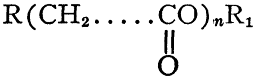
(2) 

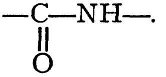
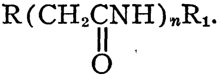
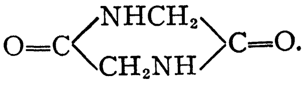
$$R\underset{\overset{\|}{CH_2}}{C}CH_2 \;\vdots\; CH_2\underset{\overset{\|}{CH_2}}{C}CH_2' \;\vdots\; CH_2\underset{\overset{\|}{CH_2}}{C}CH_2 \;\vdots\; CH_2\underset{\overset{\|}{CH_2}}{C}CH_2'\text{—}$$

The radical (1) would presumably yield 1,4–cyclohexadione  In the case of radical (2) possibly the two pairs of CH_2 groups would unite and two hydrogen atoms migrate to give the molecule:



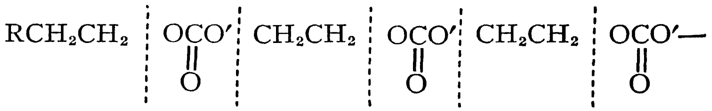
Many of the polymers that have been studied experimentally are somewhat more complicated than the foregoing examples; the rubber molecule constitutes one of the exceptions in which the unsaturation is not in a recurring side chain. The following are some examples of polymers having a recurring unsaturated side chain.

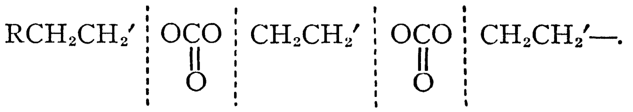
(1) Polymers containing the group  $-\underset{\underset{O}{\|}}{C}-O-$. The simplest of these polymers would be represented by the formula  $R(CH_2\underset{\underset{O}{\|}}{C}O)_nR_1$. Such a substance would be expected to yield the six membered ring glycolide  which is also found experimentally.[9a] Higher members represented by the general formula  $R(CH_2\ldots\ldots\underset{\underset{O}{\|}}{C}O)_nR_1$ should yield lactone rings.

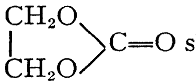
(2) Polymers containing the group  $-\underset{\underset{O}{\|}}{C}-NH-$. The simplest of these polymers would be represented by the formula  $R(CH_2\underset{\underset{O}{\|}}{C}NH)_nR_1$. On thermal decomposition it should yield the analogous compound to glycolide, namely diketopiperazine . This polymer and related ones in which the hydrogen atoms are replaced by other radicals are polypeptides, which should thus be expected to yield various homologues of diketopiperazine on decomposition at low temperatures in a high vacuum.

[9a] Carothers, *Chem. Reviews*, **8**, 353 (1931).

(3) Polymers containing the group $-O-\underset{\overset{\|}{O}}{C}-O-$. The simplest member is $R(CH_2O\underset{\overset{\|}{O}}{C}O)_nR_1$. The higher members would be represented by the formula $R(CH_2.....O\underset{\overset{\|}{O}}{C}O)_nR_1$ or $R(CH_2.....O\underset{\overset{\|}{O}}{C}OCH_2.....O\underset{\overset{\|}{O}}{C}O)_nR_1$ when the group $-O\underset{\overset{\|}{O}}{C}O-$ is not equally spaced. These polymers have been very carefully studied by Hill and Carothers[10] and have been shown to yield cyclic esters (either monomeric or dimeric) on thermal decomposition. As an example we may consider the polymer $R(CH_2CH_2O\underset{\overset{\|}{O}}{C}O)_nR_1$ which should give the radicals:

(1) 
$$RCH_2CH_2 \vdots O\underset{\overset{\|}{O}}{C}O' \vdots CH_2CH_2 \vdots O\underset{\overset{\|}{O}}{C}O' \vdots CH_2CH_2 \vdots O\underset{\overset{\|}{O}}{C}O'-$$

(2) 
$$RCH_2CH_2' \vdots O\underset{\overset{\|}{O}}{C}O \vdots CH_2CH_2' \vdots O\underset{\overset{\|}{O}}{C}O \vdots CH_2CH_2'-.$$

In either case it is clear that the five membered ring ethylene carbonate  should be the only product. This was found exclusively experimentally.

(4) Polymers containing the group $-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-$. These have the general formula $(RCH_2.....\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C})_nR_1$ and have also been very carefully studied;[11] they have been found to yield acid anhydrides (either monomers or dimers according to the length of the recurring unit) on decomposition in a high vacuum. The products predicted according to the foregoing rules, are in general the same

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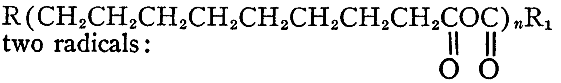
[10] Hill and Carothers, *J. Am. Chem. Soc.*, **55**, 5031 (1933).

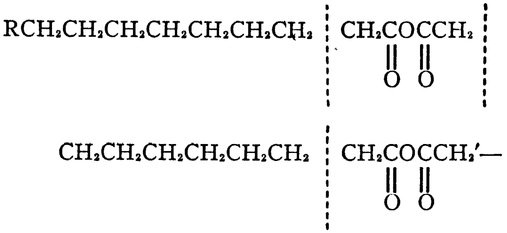
[11] Hill and Carothers, *J. Am. Chem. Soc.*, **55**, 5023 (1933).

as those found experimentally, with the exception of the theoretical prediction that succinic anhydride should be a frequent product in the decomposition of these polymers. It does not seem to have been reported experimentally. For example, the polymer $R(CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C})_nR_1$ should give the two radicals:



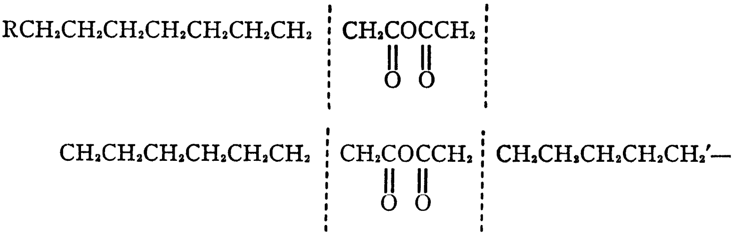
$$R(CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C})_nR_1$$

(1)



$$\begin{array}{l} RCH_2CH_2CH_2CH_2CH_2CH_2CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}CH_2 \;\vdots \\ \qquad\qquad CH_2CH_2CH_2CH_2CH_2CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}CH_2'\text{—} \end{array}$$

(2)



$$\begin{array}{l} RCH_2CH_2CH_2CH_2CH_2CH_2CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}CH_2 \;\vdots \\ \qquad\qquad CH_2CH_2CH_2CH_2CH_2CH_2 \;\vdots\; CH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}CH_2 \;\vdots\; CH_2CH_2CH_2CH_2CH_2'\text{—} \end{array}$$

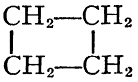
It is not quite clear why the dimer of sebacic anhydride (22 membered ring) should not be accompanied by at least some succinic anhydride and cyclohexane yet only the dimer of sebacic anhydride was reported experimentally.

CHAPTER XIII

ALICYCLIC COMPOUNDS

It has been previously pointed out (p. 79) that open chain aliphatic compounds may be regarded as composed of a succession of small unsaturated molecules linked together and terminated by methyl or ethyl groups. It is to be expected therefore that decomposition under conditions of low pressure and high temperature should yield the constituent molecules and the terminal radicals.

Alicyclic compounds can also be regarded as composed of a succession of small unsaturated molecules, but in contrast to open chain compounds there is no terminating radical since the free valencies that would normally be present when several unsaturated molecules are linked together allow mutual saturation by ring formation. The decomposition of alicyclic compounds under conditions of low pressure and high temperature should therefore result in the formation of molecules only and no radicals. This is borne out by experiment; in general, when alicyclic compounds are passed through a furnace at low pressures under conditions such that they are decomposed to an appreciable extent there is either no removal or exceedingly slow removal of metallic mirrors.[1] The following examples of some alicyclic compounds are given together with the constituent molecules of which we may regard them as being composed.

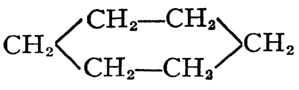


Cyclobutane

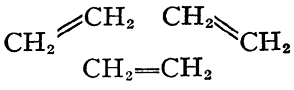
$CH_2{=}CH_2$

$CH_2{=}CH_2$

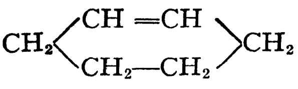
Ethylene



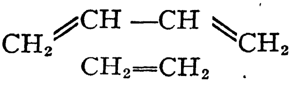
Cyclohexane



Ethylene



Cyclohexene



Ethylene + 1, 4—butadiene

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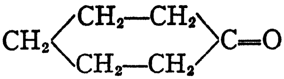
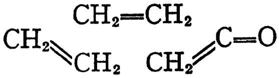
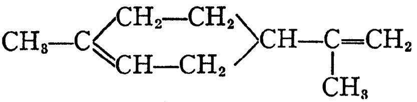
[1] Certain ring compounds, notably ethylene oxide, are exceptional in this respect.



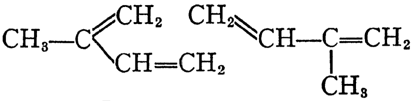
Cyclohexanone



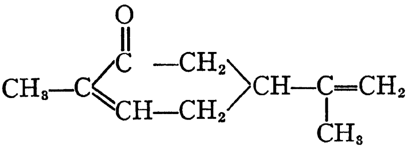
Ethylene + ketene



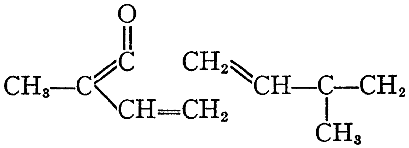
Dipentene



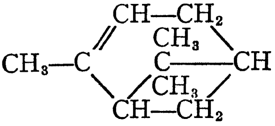
Isoprene



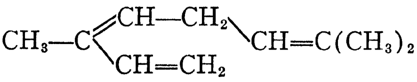
Carvone



Methyl vinyl ketene + isoprene

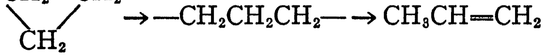


α–Pinene



Ocimene

Alicyclic carbon rings containing an odd number of carbon atoms should yield the radical —$CH_2CH_2CH_2$— (or a homologue of this radical) which probably rearranges very easily by migration of a hydrogen atom to give propylene. That this is probably the case is indicated by the striking behaviour of cyclopropane;[2] when this compound was passed through a furnace and then over a metallic mirror there was not the slightest effect on the mirror, although nearly all the cyclopropane was converted to propylene. We are inclined to represent this process as having occurred in two steps:



rather than in one process of direct isomerisation. In contrast with the behaviour of cyclopropane, ethylene oxide removes mirrors with great ease:[3] the fragments that remove the mirrors have been identified as methyl groups.[4] This behaviour may be explained according to the following scheme:

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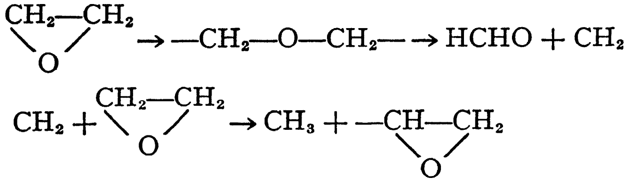
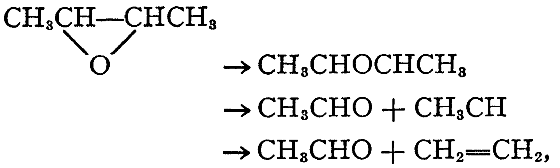
[2] Unpublished work by F. O. Rice and A. L. Glasebrook.

[3] Rice and Johnston, *J. Am. Chem. Soc.*, 56, 214 (1934).



Unlike the radical —$CH_2CH_2CH_2$—, the radical —CH_2—O—CH_2— cannot change into an isomeric molecule such as acetaldehyde by any simple sort of rearrangement; if however the primary rupture took place in a —C—O— bond instead of in a C—C bond, the radical —CH_2CH_2O— which would be produced should easily rearrange to give acetaldehyde CH_3CHO, which has been found not to remove mirrors nearly so readily as does ethylene oxide. Experiments with sym. butylene oxide to test this theory are now in progress. According to a similar scheme this compound should decompose as follows:



and therefore there should be no mirror removal at temperatures below the decomposition point of acetaldehyde.

Since in general alicyclic compounds decompose directly into compounds, the primary decomposition is not followed by a chain reaction as in the case of aliphatic compounds. This might be expected to favor the separation of molecular hydrogen in the decomposition of alicyclic compounds. If the rupture of a C—C bond (reaction I) and the separation of molecular hydrogen (reaction II),

$$RCH_2CH_2R' \rightarrow RCH_2\text{—} + R'CH_2\text{—} \qquad \text{I}$$

$$RCH_2CH_2R' \rightarrow RCH{=}CHR' + H_2 \qquad \text{II}$$

require approximately the same activation energy, both primary reactions are to be expected; however, if RCH_2CH_2R' is an aliphatic compound such as n-hexane, reaction I is followed by a chain which increases the rate perhaps 100 times but which does not produce hydrogen in appreciable amounts;[5] owing to the chain which follows reaction I, the production of hydrogen in the products, by reaction II is negligible. This effect is general for aliphatic compounds, since the chain mechanisms only seldom produce hydrogen. On the other hand, if the compound RCH_2CH_2R' is an alicyclic compound, such as cyclohexane, reaction I is not followed by a chain, and therefore the relative rates of the two reactions are determined by their relative activation energies: these we have assumed to be approximately equal, and consequently hydrogen is a major reaction product.

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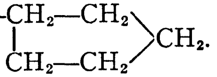
[4] F. O. Rice and E. Rodowskas, Unpublished work.

With these considerations in mind we can proceed to discuss the products to be expected in the thermal decomposition of cyclopentane and cyclohexane, both of which have recently been carefully studied experimentally.[6]

Cyclopentane.—

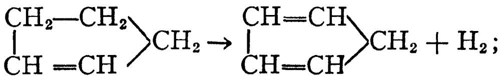


$$\text{I.}\quad C_5H_{10} \rightarrow -CH_2CH_2CH_2CH_2CH_2-$$
$$\rightarrow CH_2{=}CH_2 + -CH_2CH_2CH_2-$$
$$\rightarrow CH_2{=}CH_2 + CH_3CH{=}CH_2,$$

$$\text{II.}\quad C_5H_{10} \rightarrow C_5H_8 + H_2.$$

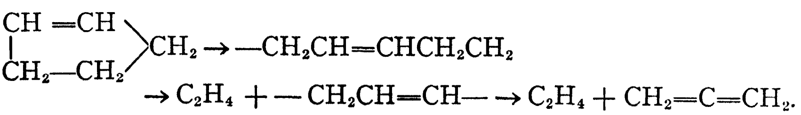
When cyclopentane is decomposed, therefore, to a very small extent only, approximately equal amounts of ethylene, propylene, cyclopentene and hydrogen should be produced. The extent of decomposition must, however, be kept small because the cyclopentene originally formed probably dehydrogenates to cyclopentadiene easily:

III.



furthermore, ethylene and allene may be formed from the cyclopentene by rupture of a C—C bond:

IV.



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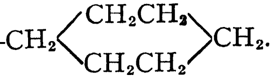
[5] Rice, *J. Am. Chem. Soc.*, **55**, 3035 (1933).

[6] Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

The products found experimentally[6] for 10% decomposition of cyclopentane at 574° and 76 mm. Hg are:

	H_2	C_2H_4	C_3H_6	C_5H_8, C_5H_6	Higher H.C.
Mole %	23	20	27	16	6

Cyclohexane.—

$$CH_2\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle CH_2.$$

$$\text{I. } C_6H_{12} \rightarrow —CH_2CH_2CH_2CH_2CH_2CH_2— \rightarrow C_2H_4$$
$$+ —CH_2CH_2CH_2CH_2— \rightarrow C_2H_4 + CH_3CH{=}CHCH_3$$

$$\text{II. } C_6H_{12} \rightarrow C_6H_{10} + H_2.$$

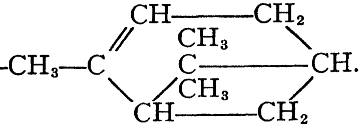
The decomposition of cyclohexane should therefore yield[7] ethylene, 2-butene, cyclohexene and hydrogen in equimolecular proportions. If more than a very small percentage of the cyclohexane is decomposed, the cyclohexene formed would be expected to undergo a further decomposition:

$$\text{III.}\qquad C_6H_{10} \rightarrow —CH_2CH{=}CHCH_2CH_2CH_2—$$
$$\rightarrow CH_2{=}CHCH{=}CH_2 + CH_2{=}CH_2$$

$$\text{IV.}\qquad C_6H_{10} \rightarrow C_6H_8 + H_2.$$

The products found experimentally for a 25% decomposition at 622° and 68 mm. pressure are:[8]

	C_2H_4	C_3H_6	C_4H_8	H_2	C_6H_{10}	C_4H_6	C_2H_6	CH_4
Mole %	20.	13.	12.	19.	5.	10.	9.	8.

Pinene.—

The literature on the thermal decomposition of pinene is very contra-

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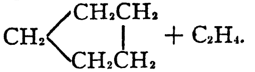
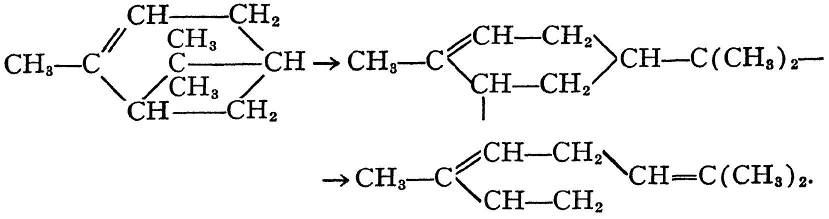
[7] There is the possibility of an alternative method of decomposition to that given by I, namely: $—CH_2CH_2CH_2CH_2CH_2CH_2— \rightarrow CH_2{=}CHCH_2CH_2CH_2CH_3$. For a seven carbon atom ring still another method of decomposition would be represented by the equation: $—CH_2CH_2CH_2CH_2CH_2CH_2CH_2 \rightarrow$ 

$$CH_2\left\langle\begin{matrix}CH_2CH_2\\ |\\ CH_2CH_2\end{matrix}\right. + C_2H_4.$$

[8] The figures have been rounded off and products occurring to less than 5% have been omitted.

dictory.[9] According to our theory one would expect a rupture of a C—C bond in the four membered ring in the beta position to the double bond to give a radical which should immediately rearrange to give the compound ocimene:



However, ocimene does not seem to be mentioned in the literature as a product of the thermal decomposition of α–pinene.

Cyclic compounds have not been investigated experimentally from the quantitative standpoint to any appreciable extent. However we can conclude tentatively from the theoretical considerations and the limited experimental evidence available that two primary side reactions normally occur: (1) a dehydrogenation process yielding, presumably without the intermediate production of a free radical, molecular hydrogen and leaving a C═C bond in the ring; (2) a rupture of a C—C bond producing a bivalent radical which either decomposes or rearranges easily into molecules. In order to avoid reaction of these bivalent radicals with the original molecules, which would initiate a chain reaction, the decomposition should be conducted at low pressures or in presence of an inert gas.

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[9] See Smith, *J. Am. Chem. Soc.*, **49**, 43 (1927); Conant and Carlson, *ibid.*, **51**, 3464 (1929); Egloff, Herman, Levinson and Dull, *Chem. Rev.*, **14**, 333 (1934).

CHAPTER XIV

REACTIONS IN THE LIQUID PHASE

The reactions of free radicals produced in the liquid phase may be expected to differ to a considerable extent from the reactions of radicals in the gaseous state. In the first place, the temperature of a liquid system (unless the reaction system is under high pressure) is limited to approximately room temperature. In gaseous systems, especially in thermal reactions, the temperature may be several hundred degrees Centigrade. The effect of this difference in temperature may be illustrated by the reactions that can occur between a methyl radical and an imaginary hydrocarbon containing one primary, one secondary and one tertiary hydrogen atom. If E_1, E_2 and E_3 are the respective activation energies of the reactions of these three hydrogen atoms with the methyl group, we may assume[1] that $E_1—E_2=1.2$ Cal. and $E_2—E_3=4$ Cal. At 600° we can calculate from the expression $e^{-(E/RT)}$ that the relative rates of the three reactions are 1: 2: 10; on the other hand at 27° the relative rates would be approximately 1: 10: 1000. It is clear, therefore, that if two possible reactions at room temperature have activation energies differing by 1–2 Cal. or more, the reaction with the lower activation energy will occur to the practical exclusion of the other. We may probably carry this reasoning a little further and assume that there is a parallelism between activation energies and bond strengths; since the strengths of the different kinds of bonds in a molecule will usually differ by at least 1–2 Cal., reaction with a radical at room temperature should involve only one kind of bond; under these conditions only one chain reaction would be expected even in the case of complicated molecules, and therefore reactions occurring through a radical chain at room temperature should be much simpler than those occurring at higher temperatures.

Effect of Solvent on Dissociation Processes.—The foregoing reasoning applies both to gaseous and to liquid systems. On the other hand, a second consideration[2] applies only to liquid systems or to gases under very high pressure. When a molecule in a gaseous phase dissociates, the two fragments fly apart and there exists only a small probability that they will collide again.[3] This however is not the case in a liquid system. The radicals or atoms formed in the primary dissociation separate with a certain amount of kinetic energy which is at once lost by collision with solvent molecules and the particles are stopped at a distance of not more than a very few molecular diameters from each other. The probability that the two particles will collide again is therefore high and may even approach one; therefore recombination should occur if the activation energy of the recombination process is either zero or very low.[4] This effect may be important in such reactions as the thermal dissociation of ethyl iodide or lead tetraethyl, when both of the products of the dissociation are molecular fragments:

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[1] Rice, *J. Am. Chem. Soc.*, 53, 1959 (1931).

[2] Franck and Rabinowitsch, *Trans. Far. Soc.*, 30, 120 (1934).

$$C_2H_5I \rightarrow C_2H_5 + I \tag{1}$$

$$(C_2H_5)_4Pb \rightarrow (C_2H_5)_3Pb + C_2H_5 \tag{2}$$

Owing to the density of molecules in the liquid state the recombination reaction may be very appreciable. It is probable that the recombination of some radicals requires an appreciable activation energy: in this case this " primary recombination " will be negligible.

We may expect therefore that in some cases, free radical production and the initiation of chains may be more difficult in the liquid than in the gaseous state and may require an activation energy sufficiently high so that the fragments will be able to penetrate many molecular layers of solvent before coming to rest. On the other hand, when one of the products of the primary dissociation is a molecule, as in the dissociation of ethyl nitrite, diazomethane, or nitrosotertbutane,

$$CH_3CH_2ONO \rightarrow NO + CH_3CH_2O \tag{3}$$

$$CH_2{=}N{\equiv}N \rightarrow N_2 + CH_2 \tag{4}$$

$$(CH_3)_3CNO \rightarrow NO + (CH_3)_3C, \tag{5}$$

the recombination may very probably be neglected.

Oxidation of Sodium Sulfite.—Before discussing liquid phase organic reactions from the free radical standpoint it seems desirable to consider first an inorganic reaction that occurs in aqueous solution, namely the oxidation of sodium sulfite. This reaction has been selected, first because it has been very carefully studied, and second because it appears probable that many organic reactions follow a similar course. It has been proved conclusively to be a chain reaction, and on the basis of the experimental evidence the further conclusion seems inescapable that the chain is carried by free radicals which are regenerated at each chain cycle; the chain finally terminates by collision of the carriers with each other.

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[3] Franck and Rabinowitsch (Ref. 2, p. 125) discuss the dissociation of a molecule RA into an atom A and a radical R. In a gas at atmospheric pressure, the atom A, after dissociation, suffers on the average over a million collisions before it collides with R. This is calculated on the assumption that A loses all its excess energy in collision with a third body at a distance equal to the mean free path.

[4] It is possible that other reactions also occur, depending on the orientation of the fragments, or steric effects or small differences in activation energy. Thus the decomposition of acetaldehyde $CH_3CHO \rightarrow CH_3 + CHO$ might be followed either by recombination to give acetaldehyde or by the reaction $CH_3 + CHO \rightarrow CH_4 + CO$.

The earlier work [5] on this reaction showed that the rate of oxidation of sodium sulfite is proportional to the concentration of sulfite and independent of the concentration of oxygen. The salts of certain heavy metals, notably of copper, accelerate the reaction to a striking degree. On the other hand many organic substances diminish the reaction rate. The more recent investigation of Bäckström [6] has been especially fruitful in that he has established that the process is one involving long reaction chains. His demonstrations, first, that ultraviolet light can replace the catalytic action of copper ions in this auto-oxidation, and second that one absorbed quantum is responsible for bringing tens of thousands of oxygen molecules into reaction, constitute the first completely convincing proof of a chain mechanism in a condensed system.[7] Bäckström also showed that the addition of hydrogen peroxide or potassium persulfate temporarily increases the rate of absorption of oxygen by an oxygen-containing solution of aqueous sodium sulfite.

The mechanism of this oxidation has very recently been subjected to detailed investigation by Franck and Haber.[8] They concluded that the reaction occurs through a free radical chain and we shall now consider the evidence for the Franck-Haber mechanism as applied to this oxidation. They explain the fact that a heavy metal, the absorbed ultraviolet light, or a foreign oxidising agent all catalyse the oxidation, by assuming that all three of these agents have one property in common, namely, that of producing a free radical which initiates a chain which goes through tens of thousands of cycles before it is finally terminated by collision between two free radicals. They conclude that the free radical initially produced by any of these methods is HSO_3, which they call monothionic acid. Their conclusion is based in the first place on Baubigny's [9] earlier study of the reaction between copper sulfate and sodium sulfite in the absence of oxygen. Reaction occurs instantaneously, cuprous hydroxide is precipitated and sodium dithionate is formed in the solution in good yield. Baubigny proposed the following mechanism:

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[5] Titoff, *Z. physik. Chem.*, **45**, 641 (1903); Reinders and Vles, *Rec. trav. chim.*, **44**, 251 (1925); a summary of the earlier work is given in "Treatise on Physical Chemistry," p. 1009, Ed. by Taylor. Van Nostrand Co., 1931.

[6] Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927).

[7] Bäckström adopted Christiansen's theory of energy chains. See Christiansen, *J. Phys. Chem.*, **28**, 145 (1924). In view of experimental evidence now available as well as certain theoretical considerations (see Franck and Rabinowitch, *Trans. Far. Soc.*, **30**, 120 (1934)) this view is probably not correct and will not be further considered.

[8] Franck and Haber, *Sitzb. preuss. Akad. Wiss.*, 250 (1931).

$$SO_3^{=} + Cu^{++} \rightarrow SO_3^{-} + Cu^{+} \qquad (6)$$

$$2\,SO_3^{-} \rightarrow S_2O_6^{=}. \qquad (7)$$

The SO_3^- is the ion of the weak acid HSO_3, which has the character of a radical and dimerises very rapidly to $H_2S_2O_6$. Friessner found that if an aqueous solution of sulfite is electrolysed [10] using an inert anode, there is abundant formation of dithionic acid at the anode, presumably by discharge of the ion HSO_3^- and dimerisation of the radical. Good yields of dithionic acid were also obtained by irradiating oxygen-free aqueous solutions of sodium sulfite with a quartz mercury lamp, hydrogen gas being simultaneously liberated. Assuming, therefore, the initial formation of the monothionic acid HSO_3, Franck and Haber postulated for the first step in the chain:

$$HSO_3 + O_2 + SO_3^{=} + H_2O \rightarrow 2\,SO_4^{=} + OH + 2\,H^{+}. \qquad (8)$$

This may possibly be subdivided [8] into two bimolecular reactions instead of the trimolecular reaction [11] given:

$$HSO_3 + O_2 \rightarrow HSO_5 \qquad (9)$$

$$HSO_5 + SO_3^{=} + H_2O \rightarrow 2\,SO_4^{=} + OH + 2\,H^{+} \qquad (10)$$

The next step is represented by the equations:

$$OH + SO_3^{=} \rightarrow SO_3^{-} + OH^{-} \qquad (11)$$

$$SO_3^{-} + H^{+} \rightarrow HSO_3 \qquad (12)$$

in which the radical HSO_3 is regenerated and can continue the chain process. The cuprous ion produced in the original reaction (6) is converted back into the cupric state through auto-oxidation and initiates new reaction chains; on the other hand the chains are broken by collision of the radicals HSO_3 and OH to form either the dimers by collision of like radicals or sulfuric acid by collision of the two unlike radicals. This chain mechanism is in agreement with the experimental fact that the chains do not occur in either strongly acid or strongly alkaline solution. In acid solution the $SO_3^=$ ions (essential for step (10) or (11)) are absent; in strongly akaline solution the essential carrier of the chain HSO_3 is absent.

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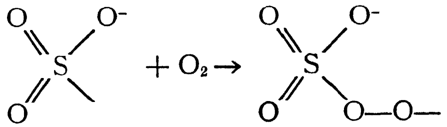
[9] Baubigny, *C. r.*, **154**, 701 (1912) ; *Ann. chim.*, **1**, 201 (1914).

[10] Friessner, *Z. Elektrochem.*, 10, 265 (1904).

[11] The water is not considered a specific component since it is present in such high concentration in aqueous solution.

On the basis of this chain mechanism [8] one would expect that a dissolved ferric salt could replace the cupric salt, even with increased effect, in producing monothionic acid from sulfites. This assumption seems logical on the basis of the greater oxidising power of the tervalent iron as compared with the divalent copper. However, ferric salts do not catalyse the oxidation of sodium sulfite. This was found to be due to the formation of a ferric-complex, from which the ferric iron can be precipitated by alkali, days or hours later according to the acidity. Since this complex formation prevents reduction of the ferric ion and consequent formation of the HSO_3, catalysis by ferric salts does not occur.

Very recently Bäckström has made a further study [12] of the sulfite oxidation and has concluded that some modification of the Franck-Haber mechanism is necessary to account for the variation in rate with hydrogen ion concentration [12a] as well as to account for the inhibiting action of alcohols. Bäckström proposes that the primary reaction (6) which produces monothionic acid ions, SO_3^-, is followed by the reaction:

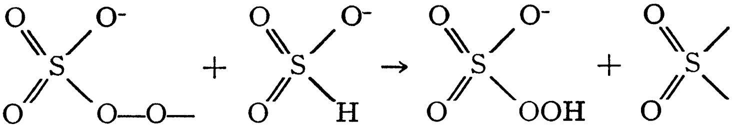


(9a)

The sulfur atom of the SO_3^-, is represented as having a free valency which is satisfied by reacting with oxygen to form the peroxide radical SO_5^-; this in turn reacts with a bisulfite ion according to the following equation:

[12] Bäckström, *Z. physik. Chem.*, **B**, **25**, 122 (1934).

[12a] See also Haber and Wansbrough-Jones, *Z. physik. Chem.*, **B**, **18**, 103 (1932).



(10a)

Since the original SO_3^- radical is regenerated, equations (9a) and (10a) constitute a complete chain cycle which produces the ion HSO_5^- of Caro's acid. This ion is supposed to react quickly with the sulfite to form the sulfate which is the final product.

The observed relation between the p_H of the solution and the rate of oxidation also lends support to this mechanism; it seems particularly reasonable in view of the fact that an alcohol present during the oxidation of sodium sulfite is converted to an aldehyde. Presumably the alcohol molecule can enter into the chain reaction by replacing the HSO_3^- in reaction (10a); however since the alcohol is an inhibitor, this chain must be shorter than the pure sulfite chain.

Haber-Willstätter Chain Mechanism.—After this brief resumé of the sodium sulfite oxidation we can pass to a consideration of a paper by Haber and Willstätter[13] on the mechanism of numerous organic oxidation and reduction processes, particularly of those which take place in aqueous solution. Their mechanism is essentially that proposed for the sulfite oxidation; a free radical is formed initially from the substrate by univalent catalytic reduction and this free radical induces a chain which gives the final products and in which the free radical is regenerated at the end of each cycle. This process is interrupted when two similar radicals react, either with dimerisation or disproportionation, or when two unlike radicals react to form the addition product, in either case removing two radicals from the chain. The same result can be accomplished by an inhibitor. It seems best to present first the original Haber-Willstätter scheme for the different classes of reactions and afterwards discuss some modifications that seem desirable in the light of subsequent work.

The general aim and limitation of the paper are best illustrated by quoting the opening paragraph: " In the following pages we shall give a picture of the course of numerous oxidation and reduction processes, in particular of those which take place in water solution and which have had previously an entirely different explanation. We will first show an inter-relationship between the large number of observations applying to this picture. The proof in individual cases will not be given, and those individual proofs which stand out require further work from a large group of chemists, some organic, some physical."

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[13] Haber and Willstätter, *Ber.*, **64**, 2844 (1931).

Bäckström had already shown in connection with his study of the sulfite oxidation [14] that there is a marked parallelsim between this reaction and the oxidation of liquid benzaldehyde and enanthaldehyde. These reactions also have high quantum yields and small quantities of certain substances inhibit both the thermal and photochemical oxidations. Furthermore both Kuhn and Meyer [15] on the one hand and Raymond [16] on the other hand have shown the importance of heavy metal ions in connection with the auto-oxidation of benzaldehyde. It seems very probable therefore that the benzaldehyde oxidation proceeds through a free radical scheme similar to that of the sulfite oxidation.

Cannizzaro Reaction.—Furthermore Haber and Willstätter have extended this idea to the Cannizzaro reaction [17] and have suggested that this reaction also proceeds through a radical chain, rather than through a direct molecular mechanism.[18] From the free radical standpoint the Cannizzaro disproportionation differs from the auto-oxidation only in the absence of elementary oxygen; the introductory reaction and the organic radicals concerned are the same. It is assumed therefore that the disproportionation in absence of oxygen is also dependent on minute quantities of a heavy metal; the high concentration of alkali required for the Cannizzaro reaction is effective because it favors the initial reduction of the benzaldehyde by keeping the H^+ concentration low. The mechanism proposed is then (where M^{+++} is a heavy metal ion):

$$C_6H_5CHO + M^{+++} \rightarrow C_6H_5\overset{|}{C}O + M^{++} + H^+ \qquad \textbf{(13)}$$

$$C_6H_5\overset{|}{C}O + C_6H_5CHO + H_2O \rightarrow C_6H_5COOH + C_6H_5\overset{|}{C}HOH \qquad (14)$$

$$C_6H_5\overset{|}{C}HOH + C_6H_5CHO \rightarrow C_6H_5CH_2OH + C_6H_5\overset{|}{C}O \qquad (15)$$

Nature of Enzymes.—In the majority of the reactions considered by Haber and Willstätter, the catalyst which splits off a hydrogen atom from the substrate and produces a free radical in the primary step, is an enzyme. These enzymes or ferments are regarded[19] as peculiarly active ferri-forms; the primary reaction may be written,

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[14] (a) Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927); (b) *idem.*, *Z. physik. Chem.*, **25 B**, 99 (1934).

[15] Kuhn and Meyer, *Naturwiss.*, **16**, 1028 (1928).

[16] Raymond, *J. chim. phys.*, **28**, 317, 421, 480 (1931).

[17] Cannizzaro, *Ann.*, **88**, 129 (1853); Meyer, *Ber.*, 14, 2394 (1881).

[18] See Fry, Uber and Price, *Rec. trav. chim.*, **50**, 1060 (1931) for references.

$$RH + [Fe^{+++}] \rightarrow R + [Fe^{++}] + H^+. \qquad (16)$$

$$\text{Substrate} + \text{Enzyme} \rightarrow \text{Radical} + \text{Monodesoxyenzyme} + H^+$$

The regeneration of the monodesoxyenzyme $[Fe^{++}]$ formed in this primary reaction is accomplished either through (1) independent autooxidation by elementary oxygen present or (2) reoxidation in the presence of the substrate (S) according to the scheme,

$$[Fe^{++}] + O_2 + S + H_2O \rightarrow [Fe^{+++}] + SO + OH^- + OH, \qquad (17)$$

in which the energy associated with the oxidation of the substrate is utilised, or (3) reoxidation, in those cases in which elementary oxygen is not available, by an oxidising agent such as a peroxide or quinone, or (4) reoxidation by such radical reactions as,

$$[Fe^{++}] + R + H_2O \rightarrow [Fe^{+++}] + OH^- + RH, \qquad (18)$$

which would interrupt the original chain. The application of these ideas to the detailed chain mechanisms for various organic reactions will now be considered.

Oxidation of Ethyl Alcohol.—Haber and Willstätter consider the oxidation of ethyl alcohol by an oxidase as an example of an organic reaction parallel to the oxidation of inorganic sulfites. Presumably a preliminary reaction between the enzyme $[Fe^{+++}]$ and the alcohol generates a radical, the monodesoxyenzyme $[Fe^{++}]$ and H^+ as follows:

$$CH_3CH_2OH + [Fe^{+++}] \rightarrow CH_3\overset{|}{C}HOH + [Fe^{++}] + H^+ \qquad (19)$$

This is followed by the chain reactions:

$$CH_3\overset{|}{C}HOH + CH_3CH_2OH + O_2 \rightarrow 2\,CH_3CHO + OH + H_2O \qquad (20)$$

$$OH + CH_3CH_2OH \rightarrow CH_3\overset{|}{C}HOH + H_2O. \qquad (21)$$

In order to avoid the three body collision required by equation (20)

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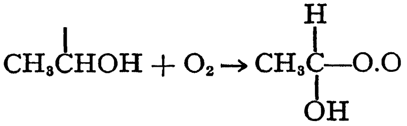
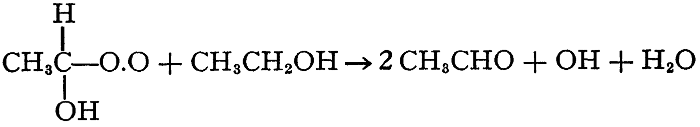
[19] This view is based on the work of Warburg, *Ber.*, **58**, 1001 (1925); *idem.*, *Biochem. Z.*, **189**, 354 (1927); Zeile and Hellström, *Z. physiol. Chem.*, **192**, 171 (1930); Kuhn, Hand and Florkin, *Z. physiol. Chem.*, **201**, 255 (1931).

Haber and Willstätter suggest a modified chain in which a peroxide radical is formed as an intermediate:



$$\mathrm{CH_3\overset{|}{C}HOH + O_2 \rightarrow CH_3\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{—}O.O} \qquad (22)$$



$$\mathrm{CH_3\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{—}O.O + CH_3CH_2OH \rightarrow 2\,CH_3CHO + OH + H_2O} \qquad (23)$$

It was not found possible to decide between the two alternative mechanisms; equations (20) and (21) demand that the peroxide radical be destroyed in the same collision in which it is formed, whereas equations (22) and (23) permit the peroxide radical to form without the action of the substrate and to exist until it collides with a substrate molecule.

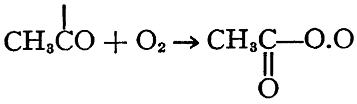
Oxidation of Acetaldehyde.—The oxidation of acetaldehyde can be explained by a chain mechanism very similar to that proposed for ethyl alcohol. There is a primary dehydrogenation followed by the chain reaction:

$$\mathrm{CH_3CHO + [Fe^{+++}] \rightarrow CH_3\overset{|}{C}O + [Fe^{++}] + H^+} \qquad (24)$$

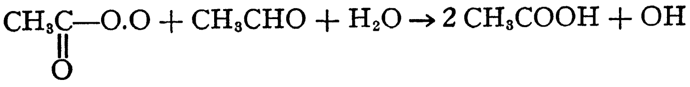
$$\mathrm{CH_3\overset{|}{C}O + CH_3CHO + O_2 + H_2O \rightarrow 2\,CH_3COOH + OH} \qquad (25)$$

$$\mathrm{OH + CH_3CHO \rightarrow CH_3\overset{|}{C}O + H_2O} \qquad (26)$$

Here also an alternative scheme is suggested to avoid the high order reaction (25):

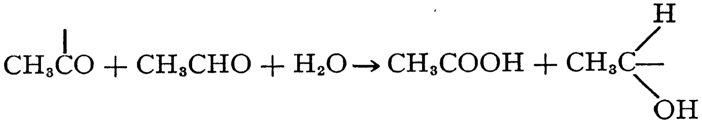


$$\mathrm{CH_3\overset{|}{C}O + O_2 \rightarrow CH_3\underset{\underset{O}{\|}}{C}{—}O.O} \qquad (27)$$

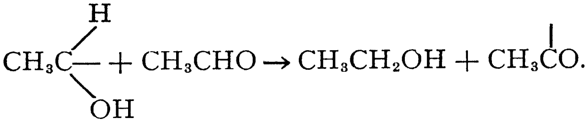


$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}{—}O.O + CH_3CHO + H_2O \rightarrow 2\,CH_3COOH + OH} \qquad (28)$$

Disproportionation of Aldehydes.—Haber and Willstätter also consider the chain mechanism that follows the generation of a free radical by reaction (24) when oxygen is absent. In this case:



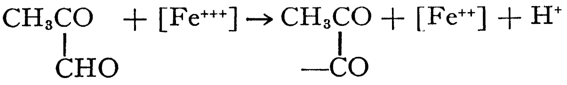
$$\mathrm{CH_3\overset{|}{C}O + CH_3CHO + H_2O \rightarrow CH_3COOH + CH_3C}{\begin{array}{l}\diagup \mathrm{H}\\ —\\ \diagdown \mathrm{OH}\end{array}} \tag{29}$$



$$\mathrm{CH_3C}{\begin{array}{l}\diagup \mathrm{H}\\ —\\ \diagdown \mathrm{OH}\end{array}} \mathrm{+ CH_3CHO \rightarrow CH_3CH_2OH + CH_3\overset{|}{C}O.} \tag{30}$$

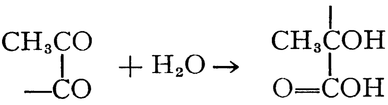
The conditions of the experiment, in particular the presence or absence of oxygen, determine whether the enzyme shall cause auto-oxidation or disproportionation. Equations (29) and (30) represent the anaerobic chain which, it will be seen, does not differ essentially from the mechanism in the presence of oxygen.

Haber and Willstätter have proposed the transformation of methyl glyoxal into lactic acid as another example of an intermolecular disproportionation activated by an enzyme. The initial reaction suggested is:

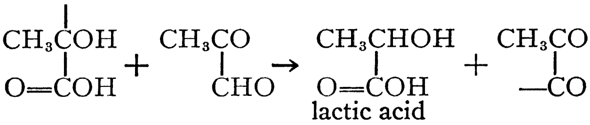


$$\begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{CHO}\end{array} + [\mathrm{Fe^{+++}}] \rightarrow \begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{—CO}\end{array} + [\mathrm{Fe^{++}}] + \mathrm{H^+} \tag{31}$$

This is followed by the chain:

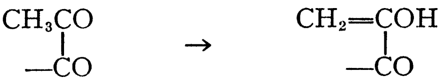


$$\begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{—CO}\end{array} + \mathrm{H_2O} \rightarrow \begin{array}{c}\mathrm{CH_3\overset{|}{C}OH}\\ |\\ \mathrm{O{=}COH}\end{array} \tag{32}$$

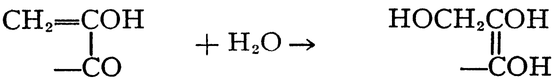


$$\begin{array}{c}\mathrm{CH_3\overset{|}{C}OH}\\ |\\ \mathrm{O{=}COH}\end{array} + \begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{CHO}\end{array} \rightarrow \underset{\text{lactic acid}}{\begin{array}{c}\mathrm{CH_3CHOH}\\ |\\ \mathrm{O{=}COH}\end{array}} + \begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{—CO}\end{array} \tag{33}$$

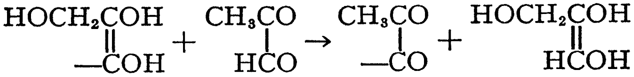
According to Haber and Willstätter the radical $\begin{array}{c}\mathrm{CH_3CO^{\cdot}}\\ |\\ \mathrm{—CO}\end{array}$ (equation (31) may also undergo other reactions than those represented by equations (32) and (33). The following chain would produce glycerine aldehyde:



$$\begin{array}{c}\mathrm{CH_3CO}\\ |\\ \mathrm{—CO}\end{array} \rightarrow \begin{array}{c}\mathrm{CH_2{=}COH}\\ |\\ \mathrm{—CO}\end{array} \tag{34}$$



$$\begin{array}{c}\mathrm{CH_2{=}COH}\\ |\\ \mathrm{—CO}\end{array} + \mathrm{H_2O} \rightarrow \begin{array}{c}\mathrm{HOCH_2COH}\\ \|\\ \mathrm{—COH}\end{array} \tag{35}$$

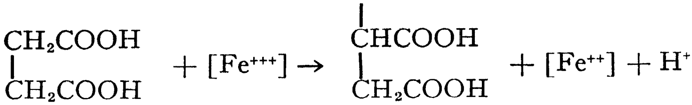


$$\begin{matrix}\text{HOCH}_2\text{COH}\\ \|\\ \text{—COH}\end{matrix} + \begin{matrix}\text{CH}_3\text{CO}\\ |\\ \text{HCO}\end{matrix} \rightarrow \begin{matrix}\text{CH}_3\text{CO}\\ |\\ \text{—CO}\end{matrix} + \begin{matrix}\text{HOCH}_2\text{COH}\\ \|\\ \text{HCOH}\end{matrix}$$

(36)

They suggest that hydrogen shifts in alcohol–carbonyl compounds (e. g. sugars) may explain at least some of the reactions involved in the decomposition of carbon chains in fermentation reactions.

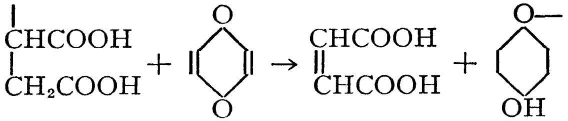
Dehydrogenation of Succinic Acid.—Still another type of chain process occurs when certain reactions are conducted in the presence of a "hydrogen acceptor" such as quinone, methylene blue or sodium nitrate. The conversion of succinic acid into fumaric acid by an enzyme [20] in presence of quinone may serve as an example. The first step is as before, the removal of a hydrogen atom from the succinic acid by the enzyme, which is again represented as [Fe^{+++}]:



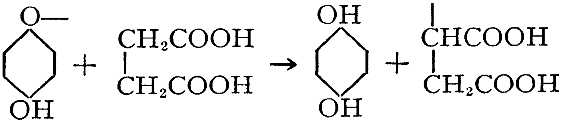
$$\begin{matrix}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\end{matrix} + [\text{Fe}^{+++}] \rightarrow \begin{matrix}|\\ \text{CHCOOH}\\ |\\ \text{CH}_2\text{COOH}\end{matrix} + [\text{Fe}^{++}] + \text{H}^+$$

(37)

The chain now involves the quinone which is finally reduced to hydroquinone through the meri-quinoid radical [21] according to the following mechanism:



(38)



(39)

Mechanism of Peroxidase Catalysis.—The activity of a group of enzymes (the peroxidases), the members of which do not themselves decompose hydrogen peroxide, but which can bring about the oxidation of certain organic substances by hydrogen peroxide, can also be represented by the Haber-Willstätter mechanism. The initial reaction in the case of pyrogallol is:

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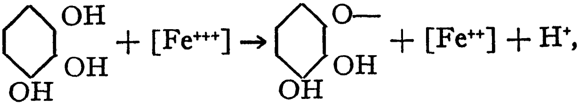
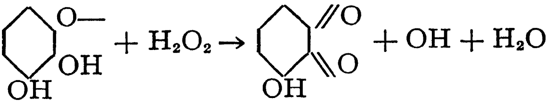
[20] Thunberg, *Skand. Arch. Phys.*, **35**, 163 (1917).

[21] See Willstätter and Piccard, *Ber.*, **41**, 1458, 3245 (1908); *idem., ibid.*, **42**, 1902 (1909); Weitz, *Z. Elektrochem.*, **34**, 538 (1928); Michaelis, *J. Am. Chem. Soc.*, **53**, 2953 (1931).

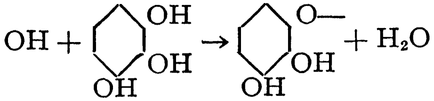


(40)

and is followed by the chain:



(41)



(42)

The hydroxy-o-quinone goes over into purpurogallin.[22]

Catalase Decomposition of Hydrogen Peroxide.—On the other hand the enzyme catalase is regarded as a specific dehydrogenase for the substrate hydrogen peroxide. The primary reaction is represented as:

$$H_2O_2 + [Fe^{+++}] \rightarrow HO_2 + [Fe^{++}] + H^+, \quad (43)$$

followed by the chain,

$$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH \quad (44)$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \quad (45)$$

In concluding their consideration of the mechanism of these reactions, Haber and Willstätter state " We hope that our concept of the production of univalent radicals and of the chain reaction of these unsaturated radicals will have indicated an organic chemical reaction principle which will explain some fields better than the assumption that the reactions proceed along molecular lines, which was made simply because both the initial and end products are molecular."

Alcohol Reactions.—Several publications bearing on the Haber-Willstätter scheme have appeared, especially in connection with the oxidation of alcohols and aldehydes. However, before considering this work it seems desirable to compare equation (19) postulated as the primary reaction between ethyl alcohol and an enzyme, with two other possible primary reactions:

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[22] Willstätter and Heiss, *Ann.*, **433**, 17 (1923).

$$CH_3CH_2OH + [Fe^{+++}] \rightarrow CH_3\overset{|}{C}HOH + [Fe^{++}] + H^+ \tag{19}$$

$$CH_3CH_2OH + [Fe^{+++}] \rightarrow CH_3CH_2\overset{|}{O} + [Fe^{++}] + H^+ \tag{19a}$$

$$CH_3CH_2OH + [Fe^{+++}] \rightarrow \overset{|}{C}H_2CH_2OH + [Fe^{++}] + H^+ \tag{19b}$$

Since it seems to be necessary to select reaction (19) as the primary step in order to have the chain products agree with experiment, it is necessary to account for the apparently arbitrary neglect of reactions (19a) and (19b). This point has already been considered in the early part of this chapter; the Haber-Willstätter mechanism is based on the implicit assumption that the activation energy of reaction (19) is at least 1–2 Cal. lower than that of either reaction (19a) or (19b); this in turn probably is determined by the relative strengths of the three kinds of hydrogen bonds in the molecule. Since the O—H bond is probably somewhat stronger (> 2 Cal.) than any C—H bonds, reaction (19a) is eliminated and since, furthermore, a primary C—H bond is about 1.2 Cal. stronger than a secondary C—H bond we are left with reaction (19) as the predominating one for the primary step. Following this line of reasoning, the predominating reaction between isoamyl alcohol and an enzyme should be represented by the equation:

$$(CH_3)_2CHCH_2CH_2OH + [Fe^{+++}] \rightarrow (CH_3)_2\overset{|}{C}CH_2CH_2OH + [Fe^{++}] + H^+ \tag{19c}$$

The removal of the more loosely bound tertiary hydrogen atom would be expected to be the predominating reaction.

The Haber-Willstätter mechanism for the oxidation of ethyl alcohol has been put to experimental test by Taylor and Gould.[23] Small amounts of hydrogen peroxide were added to 95% aqueous alcohol and the solution was illuminated[24] by a quartz mercury lamp. The rate of absorption of oxygen was much more rapid than when the hydrogen peroxide was absent, indicating that a fragment (OH or HO_2) formed by the photochemical decomposition of the hydrogen peroxide catalyses the reaction. The amount of increase in rate, however, indicated that the chains must be short;[25] nevertheless these experiments have proved that a chain mechanism for the oxidation of ethyl alcohol is a justifiable one. On the other hand, experiments on the oxidation of mannitol[26] showed that it is not catalysed by radicals produced in the photochemical decomposition of hydrogen peroxide and appears, therefore, not to be a chain reaction.

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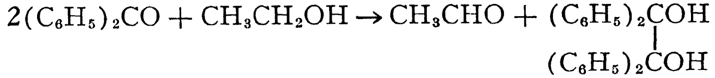
[23] Taylor and Gould, *J. Phys. Chem.*, 37, 367 (1933).

[24] Separate experiments showed that there was no appreciable absorption of oxygen without illumination.

The photosensitised oxidation of alcohols probably occurs through a free radical mechanism, but it seems difficult to reconcile any such mechanism with either the observed kinetics of the reaction or the Haber-Willstätter scheme. For example, if a solution of benzophenone in an alcohol is exposed to sunlight[27] in absence of air, the alcohol is oxidised to the aldehyde or ketone and the benzophenone is reduced to benzopinacol. The stoichiometric equation representing the reaction for a solution of benzophenone in ethyl alcohol is:



$$2(C_6H_5)_2CO + CH_3CH_2OH \rightarrow CH_3CHO + \begin{array}{c}(C_6H_5)_2COH\\ |\\ (C_6H_5)_2COH\end{array} \qquad (46)$$

On the basis of the Haber-Willstätter scheme one might assume the primary formation of the radicals $(C_6H_5)_2\overset{|}{C}OH$ and $CH_3\overset{|}{C}HOH$ resulting from a collision of an activated benzophenone molecule with an alcohol molecule. However, any free radical scheme must be in agreement with the experimental fact that the reaction is kinetically of the third order;[28] there is also the further difficulty that the same amount of alcohol is oxidised to aldehyde whether oxygen is present or not, whereas according to reaction (20) a chain reaction might be expected in presence of oxygen.[29]

Aldehyde Reactions.—Recently Wieland and Richter[30] have shown that the oxidation of acetaldehyde or benzaldehyde goes through the corresponding peracid even in dilute aqueous solution, whereas Haber and Willstätter assumed that acetic or benzoic acid is formed directly. Since, for example, peracetic acid seems to be a relatively stable molecule in aqueous solution, it is obviously necessary to modify equation (28) of the Haber-Willstätter chain as follows:

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[25] On the basis of certain calculations, Haber and Willstätter suggest a chain length of approximately 10^6 for this and similar reactions.

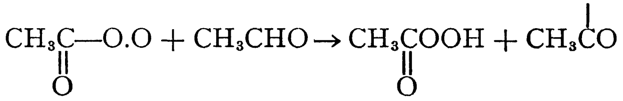
[26] Salley, *J. Phys. Chem.*, **38**, 447, 465 (1934).

[27] Ciamician and Silber, *Ber.*, (a) **33**, 2911 (1900); (b) **39**, 243 (1920). Cohen, *Rec. trav. chim.*, (a) **38**, 72, 113 (1919); (b) **39**, 243 (1920).

[28] Böeseken, *Rec. trav. chim.*, **40**, 433 (1921).

[29] See Bäckström, *Z. Phys. Chem.*, **B, 25**, 99 (1934), for a more complete discussion of this work.

[30] Wieland and Richter, *Ann.*, (a) **486**, 226 (1931); (b) **495**, 284 (1932).



$$\underset{\underset{O}{\|}}{CH_3C}\text{—}O.O + CH_3CHO \rightarrow \underset{\underset{O}{\|}}{CH_3COOH} + CH_3\overset{|}{C}O \qquad (28a)$$

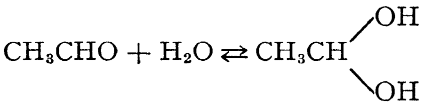
It is not known whether the peracid, as it accumulates in the system, also decomposes through a chain mechanism or whether it decomposes through one of the molecular mechanisms proposed by Wieland and Richter.[31]

There is also a further difficulty in connection with the primary reaction which may be illustrated with reference to acetaldehyde. If reaction occurs between the enzyme and the unhydrated form of the aldehyde, there are two possibilities:

$$CH_3CHO + [Fe^{+++}] \rightarrow CH_3\overset{|}{C}O + [Fe^{++}] + H^+ \qquad (24)$$

$$CH_3CHO + [Fe^{+++}] \rightarrow \overset{|}{C}H_2CHO + [Fe^{++}] + H^+ \qquad (24a)$$

Furthermore, for acetaldehyde in aqueous solution we may write the equilibrium:

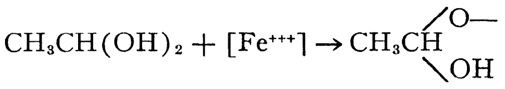


$$CH_3CHO + H_2O \rightleftarrows CH_3CH\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \qquad (47)$$

This leads to three more possible primary reactions, namely,

$$CH_3CH(OH)_2 + [Fe^{+++}] \rightarrow \overset{|}{C}H_2CH(OH)_2 + [Fe^{++}] + H^+ \qquad (24b)$$

$$CH_3CH(OH)_2 + [Fe^{+++}] \rightarrow CH_3\overset{|}{C}(OH)_2 + [Fe^{++}] + H^+ \qquad (24c)$$



$$CH_3CH(OH)_2 + [Fe^{+++}] \rightarrow CH_3CH\begin{matrix} \diagup O\text{—} \\ \diagdown OH \end{matrix} + [Fe^{++}] + H^+. \qquad (24d)$$

If any one of the five reactions (24) to (24d) has an activation energy of at least 1–2 Cal. less than any other, it should occur practically exclusively; possibly the hydrogen atom involved in reaction (24c) is sufficiently weakly bound that this reaction is the predominant primary step. It does not seem possible to decide between these different primary steps until more is known about the bond strengths of both acetaldehyde and 1, 1–dihydroxyethane.[32]

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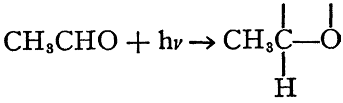
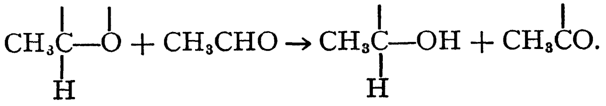
[31] See also in this connection, Bodenstein, *Sitzb. preuss. Akad. Wiss.*, 3 (1931).

The primary step in the photochemical oxidation of aldehydes has been postulated by Bodenstein [31] as:



$$\mathrm{CH_3CHO} + h\nu \rightarrow \mathrm{CH_3}\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\!-\!\overset{|}{\mathrm{O}}. \qquad (48)$$

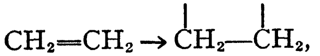
In a recent publication on the chain mechanism of the auto-oxidation of aldehydes Bäckström [33] also adopts this primary reaction, in which an aldehyde molecule with an " erect " double bond is formed. He assumes that this active form of the aldehyde can react with another aldehyde molecule according to the equation:



$$\mathrm{CH_3}\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\!-\!\overset{|}{\mathrm{O}} + \mathrm{CH_3CHO} \rightarrow \mathrm{CH_3}\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\!-\!\mathrm{OH} + \mathrm{CH_3}\overset{|}{\mathrm{C}}\mathrm{O}. \qquad (49)$$

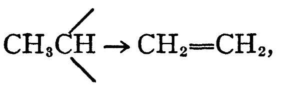
This reaction is then followed by the radical type of chain (equations (27) and (28a)) postulated by Haber and Willstätter.

It should be noted however that experiments designed to test for the presence of molecules with " opened up " bonds gave negative results.[34] For example, when ethylene is heated at low pressures and the gas brought into contact rapidly with cold metallic mirrors,[35] there is no effect, indicating that if an ethylene molecule with opened up bonds is formed,



$$\mathrm{CH_2{=}CH_2} \rightarrow \overset{|}{\mathrm{C}}\mathrm{H_2}\!-\!\overset{|}{\mathrm{C}}\mathrm{H_2}, \qquad (50)$$

it has an exceedingly short life. Even the radical $\mathrm{CH_3}\overset{/}{\underset{\backslash}{\mathrm{C}}}\mathrm{H}$, in which a hydrogen atom must migrate according to the equation,



$$\mathrm{CH_3}\overset{/}{\underset{\backslash}{\mathrm{C}}}\mathrm{H} \rightarrow \mathrm{CH_2{=}CH_2}, \qquad (51)$$

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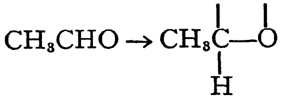
[32] Experiments by Raymond, *J. chim. phys.*, **28**, 480 (1931) and Reiff, *J. Am. Chem. Soc.*, **48**, 2893 (1926) show that the rate of oxidation of pure benzaldehyde is very definitely inhibited by small quantities of water.

[33] Bäckström, *Z. phys. Chem.*, **B**, **25**, 99 (1934).

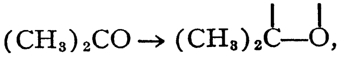
[34] These experiments do not disprove the existence of molecules with erect double bonds which may be formed in photochemical experiments.

[35] Rice and Whaley, *J. Am. Chem. Soc.*, **56**, 1311 (1934).

seems to have an exceedingly short life because it could not be detected[36] whereas under the same conditions the methylene radical could be readily identified.[37] Furthermore there seems to be no experimental evidence that such reactions as



$$CH_3CHO \rightarrow CH_3\overset{|}{\underset{H}{\underset{|}{C}}}\text{—}\overset{|}{O} \quad \text{or} \qquad (52)$$



$$(CH_3)_2CO \rightarrow (CH_3)_2\overset{|}{C}\text{—}\overset{|}{O}, \qquad (53)$$

occur prior to the dissociation into radicals, because the activation energy of the process producing active fragments [38] has the value to be expected if a bond were ruptured according to the equations:

$$CH_3CHO \rightarrow \overset{|}{C}H_3 + \overset{|}{C}HO \qquad (54)$$

$$CH_3COCH_3 \rightarrow CH_3\overset{|}{C}O + \overset{|}{C}H_3. \qquad (55)$$

Addition of Halogen Acids to Olefins.—It seems probable that radical chains may also sometimes occur in connection with polymerisation processes,[39] halogenations,[40] and the addition of halogen acids to unsaturated hydrocarbons.[41] We will conclude this chapter with a brief discussion of the last class of reactions.

From a study of the addition of halogen acids to unsymmetrical olefinic hydrocarbons and to their halogen derivatives Markownikoff [42] concluded that the addition occurs in such manner that the halogen atom goes to the carbon atom that is attached to the fewest hydrogen atoms. For example:

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3 \qquad (56)$$

$$CH_2{=}CHBr + HBr \rightarrow CH_3CHBr_2. \qquad (57)$$

Recent studies of Kharasch and his co-workers have shown that

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[36] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 741 (1934).

[37] Rice and Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).

[38] Rice and Johnston, *J. Am. Chem. Soc.*, **56**, 214 (1934).

[39] Carothers, Kirby and Collins, *J. Am. Chem. Soc.*, **55**, 789 (1933) ; Staudinger and Lautenschläger, *Ann.*, **488**, 1 (1931) ; Schultze, *J. Am. Chem. Soc.*, **56**, 1555 (1934).

[40] Dickinson and Leermakers, *J. Am. Chem. Soc.*, **54**, 3852 (1932) ; Schultze, *ibid.*, **56**, 1552 (1934) ; Bauer and Daniels, *ibid.*, **56**, 378, 2014 (1934) ; Booher and Rollefson, *ibid.*, **56**, 2288 (1934).

[41] See Kharasch and Hinckley, *J. Am. Chem. Soc.*, 56, 1243 (1934) for references to this work.

[42] Markownikoff, *Ann.*, **153**, 256 (1870).

Markownikoff's rule holds when the addition of hydrobromic acid to various unsaturated hydrocarbons is carried out with pure materials and in the absence of oxygen.[43] The reaction is catalysed by light and by minute quantities of the salts of certain heavy metals such as iron. We may therefore postulate the initial formation of a bromine atom either by the light or by the catalyst followed by the chain (using propylene as an example):

$$\mathrm{Br} + \mathrm{CH_3CH{=}CH_2} \rightarrow \mathrm{CH_3CHBr\overset{|}{C}H_2} \tag{58}$$

$$\mathrm{CH_3CHBr\overset{|}{C}H_2} + \mathrm{HBr} \rightarrow \mathrm{CH_3CHBrCH_3} + \mathrm{Br}. \tag{59}$$

This suggests that the rule is followed because in the chain process, the halogen atom adds to the carbon with fewest hydrogen atoms.

However, the reaction occurring according to Markownikoff's rule is usually accompanied to a greater or less degree by a second reaction in which the addition of the halogen acid occurs in the opposite way, the halogen going to the more hydrogenated carbon atom. Actually either of the two reactions may predominate according to the conditions. The second reaction is catalysed by such peroxides as ascaridole or benzoyl peroxide to such an extent that the first change may be rendered negligible. The second reaction is catalysed strongly by light. The second process must also be a chain reaction since it is inhibited by small amounts of different substances. It seems very probable that at least one of the steps in the chain must include the formation of the peroxide of the substrate, but a knowledge of the detailed mechanism must await further experimental investigation.

And in conclusion we will recapitulate a little. In this book we have put together, to the best of our ability, the present knowledge of the properties of the aliphatic free radicals, primarily actually of the methyl, ethyl, and methylene groups. In addition we have presented a certain amount of purely theoretical material concerning the rôle of free radicals in organic decompositions; in the course of a comparatively short time these hypotheses will be either confirmed or disproved. It should be clear to anyone giving any thought to the subject that the field of mechanisms of organic reactions in general is one in which an immense amount of work is waiting to be done, both experimentally and in interpretation of experimental data, and by physical as well as by organic chemists.

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[43] It can also be carried out in presence of oxygen if an inhibitor such as hydroquinone or diphenylamine is present.

APPENDIX I

ACTIVATION ENERGIES OF UNIMOLECULAR ELEMENTARY REACTIONS

There seems to be a distinct possibility that the course of the thermal decomposition of many thousands of organic compounds can be represented by a comparatively limited number of elementary reactions. For this reason it seems desirable to make a list of such reactions for the more common small molecules and radicals and to attempt to estimate the activation energies of their unimolecular decompositions.[1] It is of course evident that the interest and importance of this list is dependent on whether the simple elementary processes represented by such reactions as (12), (34), (75), (76), (143), (175) and (178) have, in general, activation energies sufficiently higher than the observed values for the overall reactions that they do not occur to an appreciable extent in comparison with the chain processes. At present we do not know the relative extents to which the direct processes and the chain processes occur; when studied from either the chemical or the kinetic standpoint both mechanisms seem to present a satisfactory picture. The discovery of an inhibitor for organic chain processes would permit a decisive experimental test of this point.[2]

In assigning values to the activation energies of the different reactions we have been guided largely by the considerations [3] discussed in Chapter VI especially on p. 82.

Compounds and Radicals containing only Carbon and Hydrogen.

		E (Cal.)	
(1)	$H_2 \rightarrow 2H$	105	± 4
(2)	$CH_4 \rightarrow H + CH_3$	100	± 6
(3)	$CH_4 \rightarrow H_2 + CH_2$	> 100	
(4′)[4]	$CH_3 \rightarrow CH_2 + H_2$	> 100	

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[1] These values may also be expected to apply to larger organic molecules and radicals since groups separated by two or more saturated carbon atoms have a negligible mutual influence. See pp. 76, 77.

[2] Some preliminary experiments (Rice and Richardson, Unpublished work) show that the rates of decomposition of certain organic compounds, such as butane, are unaffected by the presence of 1% of nitrosyl chloride. This indicates either the absence of chains or that the reaction, $CH_3 + NOCL \rightarrow CH_3Cl + NO$ requires too high an activation energy to be efficient as a chain breaker.

[3] In some cases, such as reaction (177) we have assigned a value more in accord with structural considerations than the value indicated by experiment (p. 78).

[4] The number of primes indicate the number of free valencies of the radical on the left-hand side of the equation.

		E (Cal.)	
(5′)	$CH_3 \rightarrow CH + H_2$	> 100	
(6″)	$CH_2 \rightarrow CH + H$	> 100	
(7″)	$CH_2 \rightarrow C + H_2$	> 100	
(10)	$C_2H_6 \rightarrow H + CH_3CH_2$	98	± 6
(11)	$C_2H_6 \rightarrow 2CH_3$	80	± 6
(12)	$C_2H_6 \rightarrow H_2 + C_2H_4$	$\geqslant E_{obs}$[5]	
(13)	$C_2H_6 \rightarrow H_2 + CH_3CH$	$\geqslant E_{obs}$	
(14)	$C_2H_4 \rightarrow H + CH_2{=}CH$	104	(95–115)
(15)	$C_2H_4 \rightarrow 2CH_2$	150	(140–170)
(16)	$C_2H_4 \rightarrow H_2 + CH{\equiv}CH$	$\gg 104$	
(17)	$C_2H_2 \rightarrow H + CH{\equiv}C$	> 104	
(18)	$C_2H_2 \rightarrow H_2 + C_2$	—	
(19)	$C_2H_2 \rightarrow 2CH$	210	(190–230)
(20′)	$CH_3CH_2 \rightarrow H + C_2H_4$	50	± 10
(21′)	$CH_2{=}CH \rightarrow CH{\equiv}CH + H$	50	± 20
(22″)	$CH{\equiv}C \rightarrow H + C_2$	—	
(23″)	$CH_3CH \rightarrow CH_2{=}CH_2$	5–10	
(24″)	$CH_3CH \rightarrow H_2 + CH{\equiv}CH$	$\gg$ 5–10	
(30)	$C_3H_8 \rightarrow H + CH_3CH_2CH_2$	97	± 6
(31)	$C_3H_8 \rightarrow H + CH_3CHCH_3$	95.8	± 6
(32)	$C_3H_8 \rightarrow CH_3 + CH_3CH_2$	79	± 6
(33)	$C_3H_8 \rightarrow H_2 + CH_3CH{=}CH_2$	$\geqslant E_{obs}$	
(34)	$C_3H_8 \rightarrow CH_4 + C_2H_4$	$\geqslant E_{obs}$	
(35)	$C_3H_8 \rightarrow H_2 + CH_3CH_2CH$	$\geqslant E_{obs}$	
(36)	$C_3H_8 \rightarrow H_2 + CH_3CCH_3$	$\geqslant E_{obs}$	
(37)	$C_3H_6 \rightarrow H + CH_2CHCH_2$	91	± 8
(38)	$C_3H_6 \rightarrow H + CH_3C{=}CH_2$	102	± 8
(39)	$C_3H_6 \rightarrow H + CH_3CH{=}CH$	103	± 8
(40)	$C_3H_6 \rightarrow CH_3 + CH_2{=}CH$	85	± 8
(40.1)	$C_3H_6 \rightarrow \frac{1}{3}CH_4 + \frac{1}{3}C_2H_4 + \frac{1}{3}C_6H_8$	$\geqslant E_{obs}$	
(41)	$C_3H_6 \rightarrow H_2 + CH_3C{\equiv}CH$	$> E_{obs}$	
(42)	$CH_3C{\equiv}CH \rightarrow H + CH_2CCH$	92	± 8
(43)	$CH_3C{\equiv}CH \rightarrow H + CH_3C{\equiv}C$	104	± 8
(44)	$CH_3C{\equiv}CH \rightarrow CH_3 + CH{\equiv}C$	85	± 8
(45)	$CH_3C{\equiv}CH \rightarrow CH_2{=}C{=}CH_2$	—	
(46)	$CH_2{=}C{=}CH_2 \rightarrow H + CH_2{=}C{=}CH$	104	± 8
(47)	$CH_2{=}C{=}CH_2 \rightarrow CH_2 + CH_2{=}C$	150	± 20
(48′)	$CH_3CH_2CH_2 \rightarrow CH_3 + CH_2{=}CH_2$	25	(20–35)
(49′)	$CH_3CH_2CH_2 \rightarrow CH_3CHCH_3$	> 25	
(50′)	$CH_3CH_2CH_2 \rightarrow CH_2 + CH_3CH_2$	~ 80	
(51′)	$CH_3CHCH_3 \rightarrow H + CH_3CH{=}CH_2$	45	(40–55)
(52′)	$CH_3CHCH_3 \rightarrow CH_3CH_2CH_2$	—	
(53′)	$CH_3CHCH_3 \rightarrow H_2 + CH_3CH{=}CH$	> 45	
(54′)	$CH_3CH{=}CH \rightarrow CH_3 + CH{\equiv}CH$	25	(20–35)
(55′)	$CH_3C{=}CH_2 \rightarrow H + CH_2{=}C{=}CH_2$	50	(35–70)
(56′)	$CH_3C{\equiv}C \rightarrow C_2 + CH_3$	—	
(57″)	$CH_2CH_2CH_2 \rightarrow CH_3CH{=}CH_2$	5–10	

---

[5] E_{obs} represents the experimentally measured activation energy for the decomposition of the particular compound.

		E (Cal.)	
(58″)	$CH_3CH_2CH \rightarrow CH_3CH{=}CH_2$	5–10	
(59″)	$CH_3CCH_3 \rightarrow CH_3CH{=}CH_2$	5–10	
(60‴)	$CH_2CHCH_2 \rightarrow H + CH_2{=}C{=}CH_2$	> 85	
(70)	$C_4H_{10}(n) \rightarrow H + CH_3CH_2CH_2CH_2$	96.5	± 6
(71)	$C_4H_{10}(n) \rightarrow H + CH_3CHCH_2CH_3$	95.3	± 6
(72)	$C_4H_{10}(n) \rightarrow CH_3 + CH_3CH_2CH_2$	78.5	± 6
(73)	$C_4H_{10}(n) \rightarrow 2CH_3CH_2$	78.2	± 6
(74)	$C_4H_{10}(n) \rightarrow H_2 + CH_3CH_2CH{=}CH_2$	$\geqslant E_{obs}$	
(75)	$C_4H_{10}(n) \rightarrow H_2 + CH_3CH{=}CHCH_3$	$\geqslant E_{obs}$	
(76)	$C_4H_{10}(n) \rightarrow CH_4 + C_3H_6$	$\geqslant E_{obs}$	
(77)	$C_4H_{10}(iso) \rightarrow H + (CH_3)_2CHCH_2$	96.3	± 6
(78)	$C_4H_{10}(iso) \rightarrow H + (CH_3)_3C$	92.3	± 6
(79)	$C_4H_{10}(iso) \rightarrow CH_3 + CH_3CHCH_3$	74	± 6
(80)	$C_4H_{10}(iso) \rightarrow H_2 + (CH_3)_2C{=}CH_2$	$\geqslant E_{obs}$	
(81)	$C_4H_{10}(iso) \rightarrow CH_4 + C_3H_6$	$\geqslant E_{obs}$	
(82)	$C_4H_8(1) \rightarrow H + CH_3CHCHCH_2$	89	± 8
(83)	$C_4H_8(1) \rightarrow H + CH_2CH_2CH{=}CH_2$	95	± 8
(84)	$C_4H_8(1) \rightarrow H + CH_3CH_2C{=}CH_2$	102	± 8
(85)	$C_4H_8(1) \rightarrow H + CH_3CH_2CH{=}CH$	104	± 8
(86)	$C_4H_8(1) \rightarrow CH_3 + CH_2CHCH_2$	72	± 8
(87)	$C_4H_8(1) \rightarrow CH_3CH_2 + CH_2{=}CH$	84	± 8
(88)	$C_4H_8(1) \rightarrow H_2 + CH_2{=}CHCH{=}CH_2$	$\geqslant E_{obs}$	
(89)	$C_4H_8(1) \rightarrow H_2 + CH_3CH_2C{\equiv}CH$	$> E_{obs}$	
(90)	$C_4H_8(2) \rightarrow H + CH_2CHCHCH_3$	91	± 8
(91)	$C_4H_8(2) \rightarrow H + CH_3CCHCH_3$	103	± 8
(92)	$C_4H_8(2) \rightarrow CH_3 + CH_3CHCH$	84	± 8
(93)	$C_1H_8(2) \rightarrow H_2 + CH_2{=}C{=}CHCH_3$	$> E_{obs}$	
(94)	$(CH_3)_2C{=}CH_2 \rightarrow H + CH_3C(CH_2)_2$	91	± 8
(95)	$(CH_3)_2C{=}CH_2 \rightarrow H + (CH_3)_2C{=}CH$	103	± 8
(96)	$(CH_3)_2C{=}CH_2 \rightarrow CH_3 + CH_3C{=}CH_2$	81	± 8
(97)	$CH_2{=}CHCH{=}CH_2 \rightarrow H + CHCHCHCH_2$	> 100	
(98)	$CH_2{=}CHCH{=}CH_2 \rightarrow H + CH_2CCHCH_2$	> 100	
(99)	$CH_2{=}CHCH{=}CH_2 \rightarrow 2CH_2{=}CH$	> 80	
(100′)	$CH_3CH_2CH_2CH_2 \rightarrow CH_3CH_2 + C_2H_4$	24	(20–35)
(101′)	$CH_3CHCH_2CH_3 \rightarrow CH_3 + C_3H_6$	26	(20–35)
(102′)	$(CH_3)_2CHCH_2 \rightarrow CH_3 + CH_3CH{=}CH_2$	26	(20–35)
(103′)	$(CH_3)_3C \rightarrow H + (CH_3)_2C{=}CH_2$	45	(40–55)
(104″)	$CH_2CH_2CH_2CH_2 \rightarrow CH_3CH{=}CHCH_3$	5–10	
(105″)	$CH_3CHCH_2CH_2 \rightarrow CH_3CH{=}CHCH_3$	5–10	
(106″)	$CH_3CHCH_2CH_2 \rightarrow CH_3CH_2CH{=}CH_2$	5–10	
(107″)	$CH_3CH_2CH_2CH \rightarrow CH_3CH_2CH{=}CH_2$	5–10	
(108″)	$CH_3CH_2CCH_3 \rightarrow CH_3CH_2CH{=}CH_2$	5–10	
(109″)	$CH_3CH_2CCH_3 \rightarrow CH_3CH{=}CHCH_3$	5–10	
(110‴)	$CH_3CHCHCH_2 \rightarrow H + CH_2{=}CHCH{=}CH_2$	> 84	
(111‴)	$CH_3C(CH_2)_2 \rightarrow CH_3 + CH_2{=}C{=}CH_2$	> 81	

Compounds and Radicals containing Carbon, Hydrogen and Oxygen.

		E (Cal.)
(120)	$HCHO \rightarrow H + HCO$	~100
(121)	$HCHO \rightarrow H_2 + CO$	~100

		E (Cal.)	
(122)	$CH_3OH \rightarrow H + CH_2OH$	~ 100	
(123)	$CH_3OH \rightarrow H + CH_3O$	~ 100	
(124)	$CH_3OH \rightarrow H_2 + HCHO$	$\geqslant E_{obs}$	
(125)	$CH_3OH \rightarrow CH_3 + OH$	84	± 8
(126′)	$HCO \rightarrow H + CO$	30	± 10
(127′)	$CH_2OH \rightarrow H + HCHO$	~ 50	
(128′)	$CH_3O \rightarrow H + HCHO$	~ 50	
(129′)	$CH_3O \rightarrow H_2 + HCO$	~ 50	
(140)	$CH_3CHO \rightarrow H + CH_2CHO$	92	± 8
(141)	$CH_3CHO \rightarrow H + CH_3CO$	104	± 8
(142)	$CH_3CHO \rightarrow CH_3 + HCO$	84	± 8
(143)	$CH_3CHO \rightarrow CH_4 + CO$	$\geqslant E_{obs}$	
(144)	$CH_3CHO \rightarrow H_2 + CH_2{=}CO$	$> E_{obs}$	
(145)	$CH_3CH_2OH \rightarrow H + CH_3CHOH$	95	± 6
(146)	$CH_3CH_2OH \rightarrow H + CH_2CH_2OH$	96.5	± 6
(147)	$CH_3CH_2OH \rightarrow H + CH_3CH_2O$	98	± 6
(148)	$CH_3CH_2OH \rightarrow CH_3 + CH_2OH$	80	± 6
(149)	$CH_3CH_2OH \rightarrow CH_3CH_2 + OH$	82	± 8
(150)	$CH_3CH_2OH \rightarrow H_2 + CH_3CHO$	$\geqslant E_{obs}$	
(151)	$CH_3CH_2OH \rightarrow H_2 + CH_2{=}CHOH$	$\geqslant E_{obs}$	
(152)	$CH_3OCH_3 \rightarrow H + CH_2OCH_3$	97	± 6
(153)	$CH_3OCH_3 \rightarrow CH_3 + CH_3O$	82	± 8
(154)	$CH_3OCH_3 \rightarrow CH_4 + HCHO$	$\geqslant E_{obs}$	
(155′)	$CH_3CO \rightarrow CH_3 + CO$	10	(8–20)
(156′)	$CH_3CH_2O \rightarrow CH_3 + HCHO$	25	(20–35)
(157′)	$CH_2CH_2OH \rightarrow OH + C_2H_4$	27	(20–35)
(158′)	$CH_3CHOH \rightarrow H + CH_3CHO$	45	(40–55)
(159′)	$CH_3OCH_2 \rightarrow CH_3 + HCHO$	25	(20–35)
(160‴)	$CH_2CHO \rightarrow CH_3CO$	15–30	
(161‴)	$CH_2CHO \rightarrow H + CH_2{=}CO$	60–80	
(170)	$CH_3CH_2CHO \rightarrow H + CH_3CHCHO$	91	± 8
(171)	$CH_3CH_2CHO \rightarrow H + CH_3CH_2CO$	104	± 8
(172)	$CH_3CH_2CHO \rightarrow H + CH_2CH_2CO$	97	± 8
(173)	$CH_3CH_2CHO \rightarrow CH_3 + CH_2CHO$	78	± 8
(174)	$CH_3CH_2CHO \rightarrow CH_3CH_2 + HCO$	82	± 8
(175)	$CH_3CH_2CHO \rightarrow C_2H_6 + CO$	$\geqslant E_{obs}$	
(176)	$CH_3COCH_3 \rightarrow H + CH_3COCH_2$	93	± 8
(177)	$CH_3COCH_3 \rightarrow CH_3 + CH_3CO$	84	± 8
(178)	$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO$	$\geqslant E_{obs}$	
(179′)	$CH_3CH_2CO \rightarrow CH_3 + CH_2{=}CO$	25	(20–45)
(180′)	$CH_3CH_2CO \rightarrow CH_3CH_2 + CO$	25	(20–45)
(181′)	$CH_2CH_2CHO \rightarrow HCO + C_2H_4$	25	(20–45)
(182‴)	$CH_3CHCHO \rightarrow CH_3CH_2CO$	15–30	
(183‴)	$CH_3CHCHO \rightarrow H + CH_3CH{=}CO$	60–80	
(184‴)	$CH_3COCH_2 \rightarrow CH_3 + CH_2{=}CO$	40–60	
(300)	$CH_3CH(OH)_2 \rightarrow H + CH_2CH(OH)_2$	95	± 8
(301)	$CH_3CH(OH)_2 \rightarrow H + CH_3C(OH)_2$	92	± 8
(302)	$CH_3CH(OH)_2 \rightarrow H + CH_3CH(OH)(O)$	96	± 8
(303)	$CH_3COOH \rightarrow H + CH_2COOH$	95	± 8

		E (Cal.)	
(304)	$CH_3COOH \rightarrow H + CH_3COO$	96	± 8
(305)	$CH_3COOH \rightarrow CH_3 + COOH$	84	± 8
(306)	$CH_3COOH \rightarrow CH_4 + CO_2$	$\geqslant E_{obs}$	
(307)	$CH_3COOH \rightarrow H_2O + CH_2{=}CO$	$\geqslant E_{obs}$	
(308′)	$CH_2CH(OH)_2 \rightarrow CH_3C(OH)_2$	> 25	
(309′)	$CH_2CH(OH)_2 \rightarrow CH_2{=}CHOH + OH$	25–40	
(310′)	$CH_3C(OH)_2 \rightarrow CH_2{=}C(OH)_2 + H$	45–60	
(311′)	$CH_3C(OH)_2 \rightarrow CH_3CHO + H$	45	± 8
(312′)	$CH_3CH(OH)O \rightarrow CH_3CHO + OH$	25	± 8
(313′)	$COOH \rightarrow CO + OH$	10–25	
(314)′″	$CH_2COOH \rightarrow CH_2{=}CO + OH$	40–70	
(315′″)	$CH_3COO \rightarrow CO_2 + CH_3$	40–70	

Organic Compounds and Radicals containing Nitrogen.

		E (Cal.)	
(500)	$CH_3ONO \rightarrow NO + CH_3O$	36	± 2
(501)	$CH_3ONO \rightarrow H + CH_2ONO$	90	± 8
(502)	$CH_2{=}N{\equiv}N \rightarrow CH_2 + N_2$	~ 36	
(503)	$CH_2ONO \rightarrow NO + HCHO$	0–8	
(504)	$CH_3CH_2ONO \rightarrow NO + CH_3CH_2O$	35	± 2
(505)	$CH_3CH_2ONO \rightarrow H + CH_3CHONO$	89	± 8
(506)	$CH_3CH_2ONO \rightarrow H + CH_2CH_2ONO$	95	± 8
(507)	$CH_3N{=}NCH_3 \rightarrow CH_3 + CH_3N{\equiv}N$	52	± 2
(508)	$CH_3N{=}NCH_3 \rightarrow H + CH_2N{=}NCH_3$	97	± 4
(509)	$CH_3N{\equiv}N \rightarrow N_2 + CH_3$	5–20	
(510)	$CH_2N{\equiv}NCH_3 \rightarrow CH_3 + CH_2{=}N{\equiv}N$	15–40	
(511)	$CH_3CH{=}N{\equiv}N \rightarrow N_2 + CH_3CH$	~ 34	

Relative Activation Energies.

Although the absolute values of the activation energies of the reactions listed in the foregoing section are not known with any degree of precision, it is possible to estimate certain energy differences very exactly. Small differences in energy frequently have a profound effect on the course of a chemical reaction and while estimates of the absolute values of the activation energies may vary considerably, it is not possible to change the relative values of certain reactions and yet keep agreement with the free radical scheme outlined in this book. Accordingly we give below a list of these relationships; the differences are in Cal. and should hold to about ± 10%. The reactions are listed in numerical order counting only the reaction of higher activation energy in each pair.

(10) — (11) > 6
(24″) — (23″) > 10
(30) — (31) = 1.2
(30) — (32) > 6
(30) — (70) = 0.5
(30) — (176) $\geqslant$ 2
(38) — (37) > 6
(39) — (37) > 6
(40) — (37) $\geqslant$ 6
(41) — (40.1) > 10
(49′) — (48′) $\geqslant$ 2
(50′) — (48′) $\geqslant$ 10

(53′) — (51′) > 6
(60‴) — (40) ⩾ 6
(70) — (71) = 1.2
(70) — (72) ⩾ 6
(70) — (501) ⩾ 6
(71) — (72) ⩾ 6
(72) — (73) = 0.3
(77) — (78) = 4
(83) — (82) ⩾ 6
(82) — (86) > 6
(84) — (82) > 10
(85) — (82) > 10
(87) — (86) > 6
(90) — (82) ~ 1
(90) — (94) ~ 0
(91) — (90) > 6
(92) — (86) > 6
(95) — (94) > 6
(103′) — (102′) > 6
(110‴) — (92) > 6
(111‴) — (96) > 6
(141) — (140) > 6
(144) — (143) ⩾ 10
(146) — (145) ⩾ 1.5
(147) — (145) ⩾ 1.5
(161‴) — (160‴) ⩾ 10
(171) — (170) ⩾ 6
(172) — (170) ⩾ 6
(174) — (173) ⩾ 2
(300) — (301) ⩾ 1
(302) — (301) ⩾ 1
(505) — (501) ~ 1
(511) — (23″) ≫ 6
(511) — (24″) ≫ 16

The members of each of the following groups of reactions may be expected to have approximately the same activation energy, within the ranges 5–10, 20–35 and 40–55 Cal. respectively: (A) (23″), (105″), (106″), (107″), (108″), (109″); (B) (48′), (54′), (100′), (101′), (102′), (156′), (157′), (159′), (179′), (180′), (181′), (312′); (C) (51′), (55′), (103′), (158′).

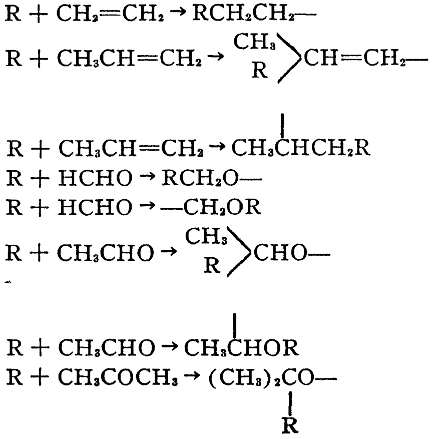
APPENDIX II

ACTIVATION ENERGIES OF ELEMENTARY BIMOLECULAR REACTIONS

We may consider four types of these reactions: (1) addition of fragments to unsaturated organic molecules. These fragments may be organic radicals or atoms such as hydrogen, oxygen, chlorine or bromine. (2) Removal of a hydrogen atom from an organic molecule by a free radical or a free atom. (3) Rupture of the skeleton of an organic molecule by a free radical or atom and (4) combination or reaction of fragments with each other.

Addition to Unsaturated Molecules.

Reactions of this type probably occur with very low activation energies. Because the resulting radicals are relatively unstable and require only about 25 Cal. of activation energy for their decomposition,[1] they are important only at relatively low temperatures (below 300°). They may be expected to occur readily in condensed systems and probably enter into the mechanism of many polymerisation processes. (See p. 181). The following are some examples in which R represents an atom or organic fragment:



$$R + CH_2{=}CH_2 \rightarrow RCH_2CH_2{—}$$

$$R + CH_3CH{=}CH_2 \rightarrow \begin{matrix}CH_3\\R\end{matrix}\!\!>CH{=}CH_2{—}$$

$$R + CH_3CH{=}CH_2 \rightarrow CH_3\overset{|}{C}HCH_2R$$

$$R + HCHO \rightarrow RCH_2O{—}$$

$$R + HCHO \rightarrow {—}CH_2OR$$

$$R + CH_3CHO \rightarrow \begin{matrix}CH_3\\R\end{matrix}\!\!>CHO{—}$$

$$R + CH_3CHO \rightarrow CH_3\overset{|}{C}HOR$$

$$R + CH_3COCH_3 \rightarrow (CH_3)_2\underset{\underset{R}{|}}{C}O{—}$$

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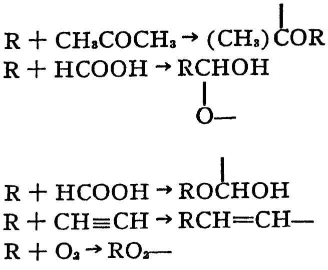
[1] See for example reactions (48') (100') (101') (102') (156') (157').



$$R + CH_3COCH_3 \rightarrow (CH_3)\overset{|}{C}OR$$

$$R + HCOOH \rightarrow R\underset{\substack{|\\ O-}}{C}HOH$$

$$R + HCOOH \rightarrow RO\overset{|}{C}HOH$$

$$R + CH\equiv CH \rightarrow RCH{=}CH-$$

$$R + O_2 \rightarrow RO_2-$$

There are practically no measurements available of the activation energies of these processes. The reactions of hydrogen atoms or methyl radicals with ethylene (pp. 25, 26, 67, 68) probably have activation energies less than 10 Cal. and the reaction $CH_3 + O_2 \rightarrow CH_3.O_2$ (pp. 29, 30) seems to have an activation energy of about 4 Cal. Possibly when R represents a hydrogen atom, the activation energy of any one of these processes lies in the range 2–10 Cal. with somewhat higher values when R is an organic radical. We may remark here also that the interest and importance of these processes depends on whether, in such reactions as the hydrogenation of ethylene to ethane, the activation energy of the chain mechanism is equal to or less that the activation energy of the direct addition of molecular hydrogen.

Removal of a Hydrogen Atom from an Organic Molecule.

The type of reaction between radicals and organic molecules which can be expressed by the equation $R + R_1H \rightarrow R_1 + RH$ seems to be the common one at temperatures above about 400°. From considerations of the mechanism of organic decompositions [2] it seems necessary to assign higher values for the activation energies of these reactions than might be expected [3] from theoretical considerations, namely in the range 15–30 Cal. It seems best at present to adopt an arbitrary and empirical method for obtaining estimates of these activation energies; the values obtained in this way seem to give satisfactory results in interpreting organic reactions on the basis of a chain mechanism. We suggest taking a value of about 20 Cal. for all these reactions plus a correction depending on the strength of the bond made, as compared with the strength of the bond broken. Since there is a parallelism between the activation energies assigned in Appendix I and bond strengths, the necessary correction can be obtained by adding the appropriate equations; the following examples are given to illustrate the method:

---

[2] See Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

[3] See London, *Z. Elektrochem.*, **35**, 552 (1929).

Reaction		Correction Cal.	E Cal.
$H + C_2H_6 \rightarrow H_2 + C_2H_5$	(10) — (1)	—7	13
$CH_3 + C_3H_8 \rightarrow CH_4 + CH_3CH_2CH_2$	(30) — (2)	—3	17
$CH_3 + C_3H_8 \rightarrow CH_4 + CH_3CHCH_3$	(31) — (2)	—4.2	15.8
$CH_3 + C_3H_6 \rightarrow CH_4 + CH_2CHCH_2$	(37) — (2)	—8	12
$CH_3 + CH_3COCH_3 \rightarrow CH_3 + CH_3COCH_2$	(176) — (2)	—5	15
$C_2H_5 + CH_4 \rightarrow C_2H_6 + CH_3$	(2) — (10)	+2	22

Rupture of Organic Molecules by Radicals.

In order to make the products calculated on the basis of a chain mechanism agree with the products found experimentally, it is necessary to exclude all reactions of the type $R + R_1R_2 \rightarrow RR_1 + R_2$. Since these reactions probably have lower activation energies than those discussed in the last paragraph it seems necessary to assume that the hydrogen atoms surrounding the carbon skeleton exert a shielding influence and slow up the rate to negligible proportions as compared with the rate of reaction of the radical with the hydrogen atoms. Assuming that these reactions require 4 Cal. less activation energy than the type mentioned in the last section, a factor of 10^{-2} to 10^{-4} would be sufficient.

Recombination and Interaction of Radicals.

These reactions have been discussed on pp. 82 and 83. An activation energy of about 8 Cal. has been assigned to all reactions of this type and in addition a steric factor of about 10^{-1} in the velocity constants of these reactions has been assumed.

INDEX OF NAMES

Allen, 35, 78, 84, 112
Altmayer, 72
Arnold, 77
Askey, 118
Avogadro, 6, 22

Bäckström, 167, 169, 171, 178, 180
Baeyer, 23
Bastet, 138
Bates, 29, 30, 31
Baubigny, 167
Bauer, 181
Belchetz, 91
Berthelot, 27
Berzelius, 21
Bettman, 122
Beutler, 19
Blacet, 27
Bodenstein, 26, 179, 180
Boeseken, 138, 178
Bone, 16
Bonhoeffer, 30
Booher, 181
Boullay, 21
Brackett, 75
Branch, 122
Bunsen, 5, 22, 61
Burk, 32

Calingaert, 126
Cannizzaro, 171
Carlson, 164
Carothers, 147, 156, 157, 181
Christiansen, 167
Ciamician, 178
Cohen, 178
Collie, 68
Collins, 181
Conant, 74, 164
Coward, 16
Cramer, 67, 68

Damon, 27
Daniels, 27, 181
Darkis, 76
Davies, 61
Dickinson, 181
Dooley, 17, 77, 91
Dull, 32, 34, 44, 59, 164
Dumas, 21
Dunstan, 68
Dushman, 84

Egloff, 164
Eilers, 124, 131
Einstein, 25
Evans, 15
Evering, 15, 32, 34, 39, 49, 56, 58, 62, 63, 83, 134, 140

Fajans, 72
Fletcher, 83, 112
Florkin, 172
Franck, 25, 165, 166, 167, 168, 169
Frankland, 5, 22
Freeman, 14
Freissner, 168
Frey, 35, 64, 65, 69, 78, 98, 162
Frolich, 94, 124
Fry, 171

Gaudechon, 27
Gault, 144
Gay-Lussac, 21
Geib, 80
Gerhardt, 22
Gershinowitz, 72, 74
Glasebrook, 18, 34, 41, 42, 50, 52, 58, 62, 71, 78, 79, 84, 152, 181
Glass, 118
Goldsby, 126
Gomberg, 23
Gould, 177
Greenberg, 109

Haber, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 180
Hague, 68
Hand, 172
Harteck, 14, 30, 80
Hartel, 19, 31, 43, 80, 81
Hein, 15
Heiss, 176
Hellerman, 49
Hellstrom, 172
Henne, 153
Henri, 27
Hepp, 64, 65, 69, 98
Herman, 164
Herzberg, 26, 28
Herzfeld, 28, 33, 56, 58, 77, 78, 80, 83, 84, 190
Hessel, 144
Hill, 31, 67, 147, 157
Hinckley, 181
Hinshelwood, 18, 83, 112, 113, 118, 136
Hofeditz, 13, 31, 33, 34, 36, 44, 55, 58, 60

Hofmann, 22
Horn, 19, 43
Hückel, W., 72, 85
Hurd, 16, 34, 62, 70, 112, 121, 122, 124, 126, 129, 131, 134, 135, 137
Hutchinson, 83, 112

Iredale, 28, 73
Ipatiew, 68

Jackson, 14
Johnston, 32, 39, 56, 58, 78, 83, 134, 152, 181
Jones, 26, 63, 67, 68, 121

Kassel, 17, 30, 72, 84, 91, 112
Kekulé, 13, 21
Kharasch, 19, 73, 76, 181
Kirby, 181
Kirkbride, 27
Kistiakowsky, 72, 74, 77, 135
Kolbe, 22
Kraus, 15
Kuhn, 145, 171, 172
Kupfer, 15, 16

Langmuir, 14
Laurent, 5, 21, 22, 23
Lautenschlager, 181
Lautsch, 18, 32, 33, 44, 50, 56, 57, 58, 77
Lavin, 14, 30
Lavoisier, 21
Lee, 15
Leermakers, 28, 35, 69, 78, 80, 81, 112, 140, 181
Leighton, 27
Levinson, 164
Lewis, 35, 88
Liebig, 21, 23
London, 190
Lucas, 19

Mackay, 14
Marek, 94, 95
Marker, 19
Markownikoff, 181, 182
Marvel, 24
Mayer, 72
McNamee, 34, 62
Meadow, 148, 152
Mecke, 18, 26, 73
Meer, 31, 83
Meinert, 34, 35, 62, 121, 124
Meyer, 171
Michaelis, 175
Midgely, 153
Mills, 73
Morgan, 61
Müller, 32

Nef, 16, 17, 90, 91
Neuhaus, 94, 95
Newman, 49
Norris, 131, 133
Norrish, 27, 28

Oldenberg, 14
Ostwald, 23

Paneth, 7, 13, 18, 24, 31, 32, 33, 34, 36, 39, 43, 44, 50, 54, 55, 56, 57, 58, 60, 61, 63, 77, 78
Pauling, 74, 112, 122
Pearson, 54
Piccard, 175
Polanyi, 19, 31, 79, 80, 81, 83
Porter, 83
Price, 171
Price, Donna, 112

Rabinowitsch, 165, 166, 167
Ramsperger, 140
Raymond, 171, 180
Reid, 148, 152
Reiff, 180
Reinders, 167
Reuter, 131, 133
Richter, 13, 178
Rice, F. O., 15, 17, 18, 19, 28, 32, 33, 34, 35, 39, 41, 42, 49, 50, 52, 56, 58, 62, 63, 70, 71, 76, 77, 78, 79, 80, 83, 84, 88, 91, 109, 112, 134, 139, 140, 152, 161, 162, 165, 180, 181, 183, 190
Rice, O. K., 90, 92
Richardson, 183
Robinson, 54
Rodowskas, 35, 50, 88, 139, 161
Rollefson, 181

Salley, 178
Salzberg, 24
Scheibe, 28
Schneider, 94, 124
Schorlemmer, 23
Schultz, 135
Schultze, 30, 32, 181
Schumacher, 28
Schweitzer, 154
Shaw, 138
Sherman, 138
Sickman, 35, 78, 84, 90, 112
Silber, 178
Simons, 32, 34, 44, 59, 62
Smallwood, 14
Smith, 164
Spence, 29, 30, 129
Staudinger, 15, 16, 154, 181
Steacie, 16, 138
Stoddart, 54

Storch, 68, 91
Style, 19, 43
Sun, 138

Taylor, 18, 25, 26, 31, 63, 67, 68, 121, 167, 177
Thenard, 21
Thiel, 72
Thompson, 113
Thunberg, 175
Titoff, 167

Uber, 171
Urey, 14
Utzinger, 50

Vles, 167
Vollrath, 17, 109

Wartenberg, 30
Waters, 109
Wansbrough-Jones, 169
Warburg, 172
Weiler, 109
Weinberg, 72
Weitz, 175
Weizel, 72
Whaley, 33, 42, 49, 62, 70, 180
Wheeler, 68
Whitmore, 46, 71
Wieland, 178
Willstätter, 50, 170, 171, 172, 173, 174, 175, 176, 177, 178, 180
Winterstein, 145
Wöhler, 21
Wood, 14
Wooster, 15

Yabroff, 122

Zeile, 172
Ziegler, 74

INDEX OF SUBJECTS

Acetaldehyde,
  decomposition of,
    in presence of azomethane, 35
    mechanism of, 89, 112, 113
    products of, 112
  erect double bonds in, 180, 181
  oxidation of, 173, 178-181
  photochemical dissociation of, 27, 28, 35, 69
Acetic acid,
  decomposition of, 135, 136
  heat of formation of, 137
Acetone,
  decomposition of,
    formation of methyl ethyl ketone in, 109
    mechanism of, 87, 109
    products of, 109
    photochemical dissociation of, 28
Acetonylacetone, formation of, from acetone, 35
Acetylene, effect of
  heat on, 33
  light on, 26
Acids, decomposition of
  acetic acid, 135, 136
  malonic acid, 136
Activation energy,
  and bond strength, 20, 71
  definition of, 71
  estimation of,
    from kinetic measurements, 77-79
    from rate of mirror removal, 78
    methods for, 82
  relative, at room temperature, 165, 166, 177, 179
  table, 78, 183-188
Activation energy of,
  dissociation of compounds into radicals, 78
  elementary reactions, 78, 80, 81, 82, 183-191
  interaction of radicals, 83, 191
  migration processes, 83, 84, 183-188
Alcohols,
  decomposition of, 134, 135
  oxidation of, 172, 173, 177
  reaction of, with benzophenone, 178
Aldehydes,
  decomposition of,
    acetaldehyde, 35, 89, 112, 113
    higher aldehydes, 113
  oxidation of, 171, 173
  photochemical dissociation of, 27
Alicyclic compounds, decomposition of, 159-163
Aliphatic azocompounds, decomposition of, 140, 141
Alkyl chlorides, decomposition of, 137, 138
Alkyl halides,
  photochemical decomposition of, 28
  reactions of,
    in Würtz synthesis, 22, 23
    with sodium vapor, 19, 31, 43, 44
Alkyl mercuric halides,
  preparation of, 47
  x-ray spectra of, 49
Alkyl nitrites,
  decomposition of, 138-140
  inhibition of chains by, 139
Allene,
  preparation of, from
    cyclopentene, 162
    decomposition of allyl radicals, 121
Allyl radical,
  decomposition into allene, 121
  from propylene, 124
  resonance in, 122
  stability of, 122, 185
iso-Amyl alcohol, oxidation of, 177
tert-Amyl alcohol, decomposition of, 135
Anaerobic chains, 173-175
Antimony, metallic,
  products of reaction with methyl or ethyl, 61
  rate of removal of mirrors of, 60
  reaction of, with radicals, 34
Arsenic triiodide, reaction of, with radicals, 59
Azocompounds,
  decomposition of,
    azoisopropane, 140, 141, 187
    azomethane, 140, 141, 187
      in presence of acetaldehyde, 35
  reaction of ethyl radicals with, 81

Benzaldehyde,
  oxidation of, 171
  photochemical dissociation of, 27
Benzophenone,
  reaction of, with alcohols, 178
Benzopinacol,
  from benzophenone, 178
Benzoyl radical, 21
Bivalent carbon radicals,
  formation of, 18, 70, 71

Bivalent carbon radicals (*continued*)
  reactivity of, 18
  rearrangement of, 16, 71, 185
Bond strengths,
  effect on, of
    adjoining double bonds, 75, 76, 82
    mutual influence of bonds, 76, 77
    substitution, 74, 75
  equivalence of bonds and, 73
  in chlorine compounds, 31
  in cyanogen, 74
  in hydrocarbons, 75
  in hydrocyanic acid, 74
  in relation to,
    activation energy, 19, 20, 72, 165
    structure, 75, 82
  of double bonds, 75
  relative, and reactions at different temperatures, 165
  table of, 75
  thermochemical estimates of, 72, 73
Butadiene, from higher olefins, 129
iso-Butane,
  decomposition of,
    mechanism of, 94
    products of, 93, 101, 102
n-Butane,
  decomposition of,
    absence of ethyl groups in, 49, 50
    by dimethyl mercury, 35
    mechanism of, 94, 101
    products of, 93
Butene-1,
  decomposition of,
    mechanism of, 125-127
    products of, 131
  isomerisation of, 126
Butene-2,
  decomposition of,
    mechanism of, 127
    products of, 131
  isomerisation of, 127
tert-Butyl alcohol,
  decomposition of,
    mechanism of, 134
    products of, 135
tert-Butyl chloride, decomposition of, 138
iso-Butyl radical, attempt to prepare, 33
n-Butyl radical, decomposition of, 64, 65, 185
sec-Butyl radical, decomposition of, 64-66, 185
iso-Butylene, 127-129
s-Butylene oxide, decomposition of, 161

Cacodyl radical, 22
Cadmium, metallic, reaction of, with radicals, 34
Cannizzaro reaction, 171
Carbon, valence of, 13, 18, 23
Carbon dioxide, as transport gas, 33, 39
Carbon monoxide,
  formation of, in radical decompositions, 108
  reaction of, with diazomethane, 15, 16
Carbon tetra-iodide, reaction of, with radicals, 44
Caro's acid, production of, in sulfite oxidation, 170
Carvone, 160
Catalase, decomposition of hydrogen peroxide by, 176
Chain initiation, by free radicals, 35. *See also* Radicals, free
Chain reactions,
  at room temperature, 165
  hydrogen acceptors in, 175
  inhibition of, 139
  in liquid phase, 165-182
  in thermal decompositions, of
    ethers, 114-119
    ketones and aldehydes, 98-113
    other organic compounds, 134-141
    paraffin hydrocarbons, 91-107
    olefins, 123-133
Chains,
  anaerobic, 173-175
  initiation of, 35
  termination of, 87, 170
Condensable gases, for transporting free radicals, 33, 39
Copper salts, effect of, on sulfite oxidation, 167, 169
Cyanogen, strength of C—C bond in, 74
Cyclic compounds, *see* Alicyclic compounds
Cyclobutane, 159
Cyclohexane,
  decomposition of, 163
  ethylene units in, 159
Cyclohexanone, 160
Cyclohexene,
  butadiene and ethylene units in, 159
  decomposition of, 163
  from cyclohexane, 163
Cycloparaffins, from radicals, 68, 85, 142
Cyclopentane, decomposition of, 162, 163
Cyclopropane, decomposition of, 160

Deactivation of metallic mirrors, 32, 34, 36, 38
Diacetyl, 64
Diallyl,
  formation of,
    from propylene, 124
    in olefin decompositions, 122

Diazomethane,
  decomposition of, 16, 187
  dissociation of, in a condensed system, 166
  ketene from, 15
  preserving, in dibutylphthalate solution, 41
  reaction with carbon monoxide, 15, 16
Dichloroethane, decomposition of, 138
Diethyl ether,
  decomposition of,
    initial rate of, 90
    mechanism of, 89, 90, 115
    photosensitised, 35
    products of, 90, 115, 116, 118, 119
Diethyl ketone, decomposition of, 110, 111
Di-isopropyl ether, 117, 119
2, 2-Dimethyl butane,
  decomposition of,
    mechanism of, 106
    products of, 99, 105
Dimethyl ditelluride, 51, 62
Dimethyl ether,
  decomposition of,
    mechanism of, 87, 115
    photosensitised, 35
    products of, 114, 115, 118, 119
Dimethyl ketene, formation of, 111
Dimethyl mercury,
  influence on decomposition of butane, 35
2, 3-Dimethyl pentane, 97-99
Dioxane, from formaldehyde polymer, 154
Dipentene,
  from rubber decomposition, 153
  isoprene units in, 160
Disproportionation,
  of aldehydes, in solution, 171, 173-175
  of radicals, 62, 63
Di-tert.-butyl ether, 117, 118
1, 3-Dithiane, from sulfur polymers, 151
1, 4-Dithiane, from sulfur polymers, 148, 149, 151
1, 3-Dithiolane, from sulfur polymers, 149
Dithionic acid, in sulfite oxidation, 168
Double bonds,
  between carbon and oxygen in ketones, 108
  effect of, on strength of adjoining bonds, 76, 120
  erect, 26, 180, 181
  strength of, 75

Einstein photochemical equivalence law, 25
Electrical production of free radicals, 14, 42
Electrolysis, and radical formation, 15, 168
Elementary reactions,
  activation energies of, 78, 80, 81, 82, 183-191
  between sodium and alkyl halides, 19, 31, 43, 44, 79
  rates of, 84-90
  steric factors in, 81, 85, 191
Enanthaldehyde, oxidation of, 167
Energy chains, in sulfite oxidation, 167
Enzymes, 171, 172
Equivalence of bonds, 73
Erect double bonds, 26, 180, 181
Ethane,
  decomposition of,
    mechanism of, 91, 92
    pattern reaction for, 86, 87, 88
    products of, 92
  strength of C—C bond in, 73, 74
Etherin radical, 21
Ethers, decomposition of, 114-119
Ethyl alcohol,
  decomposition of, 134
  oxidation of,
    in aqueous solution, 172, 173, 176-178
    photosensitised, 177, 178
  reaction with benzophenone, 178
Ethyl chloride, decomposition of, 137, 138
Ethyl groups,
  estimation of, in presence of methyl groups, 50. *See also* Ethyl radical
Ethyl iodide,
  dissociation of, in a condensed system, 166
Ethyl nitrite,
  decomposition of, 138, 139
  dissociation of, in a condensed system, 166
Ethyl radical,
  absence of, in propane and butane decompositions, 49, 50
  identification of, 44
  life of, 56
  production of, from tetraethyl lead, 33
  properties of, 33
  reaction of, with
    ethyl radicals, 82, 83
    metals, 61, 62
    molecular hydrogen, 80
  recombination of, 33, 62, 63, 66
  stability of, 45, 63, 77, 184
Ethylene,
  addition of hydrobromic acid to, 181, 182

Ethylene (*continued*)
  effect of,
    heat on, 33, 41, 43, 70
    hydrogen atoms on, 25, 26
  electrical decomposition of, 43
  erect double bonds in, 16, 70
  reaction of, with free radicals, 67, 68
Ethylene nitrite, decomposition of, 139, 140
Ethylene oxide, decomposition of, 160, 161
Ethylidene radical,
  in Nef's theory, 16
  isomerisation of, 70, 71, 184

Ferric salts, reaction of, with sodium sulfite, 169
Formaldehyde,
  effect of light on, 26
  erect double bonds in, 26
  photochemical dissociation of, 27
Formaldehyde polymer, decomposition of, 154
Free radicals. *See* Radicals, free

Gases, condensable, for transporting free radicals, 33, 39

Haber - Willstätter chain mechanism, 170-181
Halides, alkyl,
  photochemical dissociation of, 28
  reaction of, with
    alkali metals, 31
    sodium vapor, 43, 44, 19, 31, 79
  reactions in Würtz synthesis, 22, 23
Halogen acids, addition of, to olefins, 181, 182
Halogenations, occurring through radical chains, 181
Hexadecane, decomposition of, 142-145
Hexamethyl ethane, decomposition of, 142
iso-Hexane, decomposition of, 99, 104, 105
n-Hexane, decomposition of, 99, 104
Hexa-tert-butylethinylethane, 24
Hot molecules, 32
Hydrocarbons, *see* Paraffin hydrocarbonds, Olefins, Cycloparaffins, and under the individual names
Hydrocyanic acid, strength of C—H bond in, 74
Hydrogen acceptors, in chain reactions, 175
Hydrogen, atomic
  formation of,
    from lead tetramethyl, 32
    in discharge tube, 14
    using excited mercury, 25, 31
  identification of, 54
Hydrogen (*continued*)
  life of, 14
  reaction of, with
    ethylene, 25, 26
    hydrocarbons, 30, 31
    metallic mirrors, 54
    molecular hydrogen, 80
Hydrogen atoms, in organic molecules,
  effect of temperature on reactivity of, 76, 120-123
  effect of temperature on reactivity of, 165
  relative reactivity of primary, secondary, and tertiary, 70, 75, 91, 100. *See also* Activation energy, Bond strength.
Hydrogen peroxide,
  decomposition of, by catalase, 176
  effect of temperature on reactivity of, 167
  in photosensitised oxidation of ethyl alcohol, 177, 178
  oxidation of pyrogallol by, 175, 176
Hydroxyl radical, preparation of, 14

Identification of,
  atomic hydrogen, 54
  radicals, 38, 39, 44-54
Induced decomposition by free radicals, 35
Initiation of chains by radicals, 35
Inhibitors, in
  addition of hydrobromic acid to olefins, 182
  gaseous thermal decompositions, 139
  sodium sulfite oxidation, 167, 170
Interaction of radicals, activation energy of, 83
Isomerisation, of
  bivalent radicals, 71, 185, 187
  olefinic radicals, 122, 123, 185-187,
  olefins, 126-133
Isoprene, formation of, in decomposition of rubber, 153

Ketene,
  formation of, from
    acetic acid, 136
    acetone, 83, 109
    diazomethane, 15, 16
    other ketones, 109, 111
  source of methylene radicals, 41
Ketenes, formation from
    fatty acids, 136
    ketones, 108-112
Ketones, aliphatic,
  absorption spectra of, 76
  decomposition of, 108-112
  photochemical dissociation of, 27, 28

Lactone polymers, decomposition of, 156
Larger molecules, decomposition of, 142-158
Lead, metallic, combination of with radicals, 34
Lead tetraethyl,
  decomposition of,
    at higher pressures, 35
    at low pressures, 62
    products of, 35, 61, 62
  dissociation of, in a condensed system, 166
  preparation of ethyl groups from, 33
Lead tetramethyl,
  decomposition of,
    at higher pressures, 34, 35
    at low pressures, 66, 68
    products of, 34, 61, 62
  preparation of free methyl groups from, 31, 32, 36, 40, 66
  purification of, 37
Life of radicals, *see* Radicals, free.
Liquid phase, reactions in, 165-182

Malonic acid,
  decomposition of liquid, 136
  heat of formation of, 137
Mannitol, oxidation of, 177, 178
Markownikoff's rule, 181, 182
McLeod gauge, small, 46, 47
Mercuric halides, alkyl, 47, 49
Mercurous bromide, formation of, 50
Mercury, reaction of with radicals, 34, 45
Mercury dimethyl, influence of, on butane decomposition, 35
Mercury, di-n-butyl, decomposition of, 64, 65
Mercury, di-sec-butyl, decomposition of, 65, 66, 67
Metal alkyls,
  containing two metallic atoms, 62
  decomposition of, 34, 35, 64, 67
Metallic mirrors, *see* Mirrors, metallic
Metals,
  attacked by free radicals, 58
  organo, 15
  products formed by interaction with radicals, 61, 62
  temperature coefficient of reaction with radicals, 60
Methane,
  and atomic hydrogen, 30
  decomposition of, 91, 183
  effect of heat on, 33, 91
  presence of, in products of ethane decomposition, 92
  strength of C—H bond in, 72
Methyl alcohol, thermal decomposition of, 134, 186
Methyl ethyl ether, decomposition of, 114, 115, 118, 119, 186
Methyl ethyl ketone, decomposition of, 108-110
Methyl groups,
  estimation of, in presence of ethyl groups, 50. *See also* Methyl radical
Methyl iodide, photochemical oxidation of, 29
Methyl isopropyl ether, 116, 117
Methyl isopropyl ketone, decomposition of, 111
Methyl nitrite, decomposition of, 138, 139, 187
3-Methyl pentane, decomposition of, 99, 106, 107
Methyl propyl ether, decomposition of, 118, 119
Methyl propyl ketone, decomposition of, 111
Methyl radical,
  addition of, to unsaturated hydrocarbons, 120
  concentration of, in decomposing acetone, 88, 89
  identification of, 38, 44
  life of, 55
  oxidation of, 29, 30, 190
  preparation of,
    from lead tetramethyl, 31, 32, 36, 40, 66
    from organic compounds, 41
  reaction of, with
    metals, 58, 61, 62
    molecular hydrogen, 56, 80, 31
    radicals, 62
  recombination of, 62, 191
  stability of, 45, 77, 78, 184
  steric effect in reaction with molecules, 81
Methylene radical,
  absence of, in methane decomposition, 91
  formation of, from
    diazomethane, 16
  ethylene oxide, 161
  identification of, 51
  life of, 70
  preparation of, 41, 42
  reaction of, with
    metals, 42, 52, 53
    organic molecules, 42
Migrations of atoms or groups,
  activation energies of, 83, 84
  in bivalent radicals, 71, 184-186
  in decomposition of

Migrations of atoms or groups,
  in decomposition of (*continued*)
    acetaldehyde, 113
    acids, 136, 137
    olefins, 122, 123
  in fermentation reactions, 174, 175
Mirrors, metallic,
  deactivation of, 32, 34, 36, 38
  effect of temperature on, 59, 60
  formation of, by heating metal alkyls, 38
  guard, 58
  products from hot and cold mirrors, 61
  reaction of, with
    atomic hydrogen, 54, 32
    methyl radicals, 50, 34
    methylene radicals, 52, 53
  removed by free radicals, 58
Monothionic acid, in sodium sulfite oxidation, 168
Mutual influence of unsaturated groups in a molecule, 76, 77

Nef's hypothesis, 16-18
Neopentane, decomposition of, 97, 104
Nitrites, alkyl, thermal decomposition of, 138-140, 187
Nitroso-tert-butane, dissociation in a condensed system, 166
Non-volatile organic compounds, decomposition of, 147-158

Olefinic hydrocarbons,
  addition of halogen acids to, 181, 182
  decomposition of, 120-133, 184, 185
Organometallic compounds,
  containing two metallic atoms, 62. *See also* Metals, Radicals
Organometals, 15
Oxidation, of
  acetaldehyde, 173, 178-181
  benzaldehyde, 171
  ethyl alcohol, 172, 173
  methyl radicals, 29, 30, 190
  pyrogallol, 175, 176
  sodium sulfite, 166-170

Paraffin hydrocarbons,
  bond strengths in, 72-75
  decomposition of, 91-107, 145-147
  heats of combustion and formation of, 72-75
Parahydrogen, reaction with hydrogen atoms, 80
Pattern reactions, 86-90
Pentamethylene sulfide, from sulfur polymers, 152
iso-Pentane, decomposition of, 96, 100-104
n-Pentane, decomposition of, 95, 100-103
1-Pentene,
  decomposition of, 129, 130, 132
  isomerisation of, 129
2-Pentene, decomposition of, 130-132
Peracetic acid,
  formation of, in acetaldehyde decomposition, 178, 179
Peracid, formation of in autoxidations, 178, 179
Peroxidase catalysis, 175, 176
Peroxide effect, in addition of hydrobromic acid to olefins, 182
Peroxide, formation by methyl radicals, 29, 30
Persulfate, potassium, effect of, on sodium sulfite oxidation, 167
Pinacolone, decomposition of, 110-112
α-Pinene,
  decomposition of, 163, 164
  isomeric with ocimene, 160
Polymerisation,
  of ethylene,
    by hydrogen atoms, 25, 26
    by radicals, 67, 68
  through a radical chain mechanism, 181
Polymers,
  decomposition of, 147-158
  formaldehyde, 154
  isoprene, 152-154
  sulfur, 148-152
Potassium persulfate, effect of, on sodium sulfite oxidation, 167
Pressure, effect of,
  on decomposition of
    olefins, 122
    paraffins, 98
  on preparation of free radicals, 34
Propane,
  decomposition of,
    absence of ethyl groups in, 49, 50
    chain termination in, 93
    mechanism of, 92
    products of, 93, 101
Propionic aldehyde, decomposition of, 112, 113
n-Propyl radical, attempt to prepare, 33
Propylene,
  addition of hydrobromic acid to, 181, 182
  allyl radical from, 124
  decomposition of, 123-125
Pyrogallol,
  oxidation of, 175, 176

Quinone, as hydrogen acceptor, 175

Radical, definition of, 21

Radicals, free,
  condensable gases for transporting, 33, 39
  decomposition of, 62-67, 79, 142, 147
  electrical production of, 14, 42
  elementary reactions of, 82, 83
  excited, 14, 31
  formation of,
    at electrodes, 15, 168
    from sodium vapor and alkyl halides, 31, 43
    in condensed systems, 165, 166
    in discharge tube, 42
  identification of, 38, 39, 44-54
  initiation of chains by, 35
  interaction of, 77, 78
  large,
    attempts to prepare, 33, 64
    cycloparaffins from, 68, 85
    decomposition of, 64, 79, 142, 147
    stability of, 33, 63
  life of, 33, 55, 56
  preparation of, from
    non-metallic organic compounds, 41
    organometallic compounds, 36-40
  reaction of, with
    antimony, metallic, 34, 61
    arsenic triiodide, 59
    cadmium, metallic, 34
    carbon tetraiodide, 34, 44
    dyes, 59
    ethylene, 67, 68, 189
    free radicals, 82, 83, 189-191
    iodine, 43
    lead, 34
    mercury, 45, 49, 50
    metallic mirrors, 61
    metallic salts, 59
    metallic sodium, 44
    metals, 34, 58, 61
    olefins, 67, 68, 120, 189, 190
    organic molecules, 67-70, 81, 82, 85, 120, 190, 191
    solid compounds, 60
    tellurium, 50
  recombination of, on
    different surfaces, 33, 56-58
    liquid air-cooled surface, 60
  transport gas, effect of, on, 34, 56
Radical twins, 22, 23
Reactions in liquid phase, 165-182
Rearrangements,
  in fermentation reactions, 174, 175
  of bivalent radicals, 16, 71, 183-188
  of univalent radicals, 113, 183-188
  molecular, 83, 183-188
Recurring unit,
  effect of, on decomposition of large molecules, 145-148
Resonance, stability of radicals due to. 113, 121
Ring formation,
  in decomposition of large molecules, 147, 148, 154. *See also* Cycloparaffins
Rubber hydrocarbon, decomposition of, 152-154
Rupture, of carbon skeleton, by free radicals, 69, 81, 82, 85, 191

Sodium, metallic, reaction of free radicals with, 44
Sodium sulfite, oxidation of, 166-170
Sodium vapor, reaction of, with alkyl halides, 19, 22, 31, 43, 44, 79
Solvent, effect of, on dissociation into radicals, 165, 166
Stationary state concentration of radicals, 88
Steric factor, effect of, in
  cycloparaffin formation, 85, 86
  decomposition of non-volatile compounds, 147
  preventing rupture of carbon skeleton, 81, 191
Strength of bonds, *see* Bond strengths
Structure and bond strength, 75, 82. *See also* Bond strengths.
Succinic acid, dehydrogenation of, 175
Sulfite oxidation, 166-170
Sulfur polymers, decomposition of, 148-152
Surfaces, solid, recombination of radicals at, 57, 58

Tellurium, metallic,
  identification of radicals, using, 51
  reaction of, with
    atomic hydrogen, 54
    methyl, 50
    methylene, 52, 54
    radicals, 34
Telluroformaldehyde, from methylene radicals, 54
Temperature, effect of, on
  decomposition of,
    non-volatile compounds, 147
    olefins, 121
    paraffins, 100, 101
  rate of mirror removal, 59, 60
  reactions in liquid phase, 165
Tetraethyl lead, *see* Lead tetraethyl
Tetramethyl lead, *see* Lead tetramethyl
Tetramethylene sulfide, from sulfur polymers, 148, 150, 152
Thermochemical estimates of bond strengths, 72, 73
1, 4-Thioxane, from sulfur polymers, 151

Transport gas,
  effect of, on life of radicals, 33, 56
  use of a condensable, 39
Trimethyl ethylene, decomposition of, 132, 133
Triphenyl methyl, 23

Unimolecular decomposition of organic compounds, 19, 30, 183-188
Unsaturated groups, mutual influence of, 76, 77
Valence, *see* Carbon, valence of
Valence theory, 13

Water vapor, as carrier gas for radicals, 39
Würtz synthesis, 22, 23

Zinc dimethyl, preparation of, 39, 44
Zinc, metallic, reaction with radicals, 34